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WADC TECHNICAL REPORT 55-221
PART VI
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FLUORINE-CONTAINING CONDENSATION POLYMERS AND RESINS

David Knutson
John J. Kolano
John E. Wier
Edward V. Gouinlock

Hooker Chemical Corporation

Best Available Copy

APRIL 1960

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Unclassified Report

A study was made to determine the effect of fluorine and fluorine content on the thermal and oxidative stability of polyester laminating resins. The preparation of perfluoroglutaronitrile, the corresponding (over)

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WADC TECHNICAL REPORT 55-221
PART VI

FLUORINE-CONTAINING CONDENSATION POLYMERS AND RESINS

David Knutson
John J. Kolano
John E. Wier
Edward V. Gouinlock

Hooker Chemical Corporation

APRIL 1960

Materials Laboratory
Contract No. AF 33(616)-5548
Project No. 7340

WRIGHT AIR DEVELOPMENT DIVISION
AIR RESEARCH AND DEVELOPMENT COMMAND
UNITED STATES AIR FORCE
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

400 — June 1960 — 38-1067

FOREWORD

This report was prepared by the Hooker Chemical Corporation under USAF Contract No. AF 33(616)-5548. The contract was initiated under Project No. 7340, "Non-Metallic and Composite Materials", Task No. 73404, "New Chemical and Methods", and is administered under the direction of the Materials Laboratory, Directorate of Laboratories, Wright Air Development Division, with Dr. R. L. Adamczak as project engineer.

This report covers work conducted from 1 February 1959 to January 1960.

The personnel of the Hooker Chemical Corporation assigned to the project were Dr. D. Knutson, Dr. J. J. Kolano, Dr. E. V. Gouinlock, Mr. John E. Wier, Research Investigators; Mr. R. N. Deleo, Mr. A. M. Teller, Technicians.

The appendix was prepared by the Department of Chemistry, Purdue University, on the continuation of work concerned with the investigation and development of new fluorine-containing monomers suitable for condensation type polymers. This work was performed on a subcontract with the Hooker Chemical Corporation as part of Contract AF 33(616)-5548.

Personnel assigned to this project were Y. R. Dhingra and A. E. Martin, working under direct supervision of Professor E. T. McBee. Assistance was provided by Dr. H. P. Braendlin.

ABSTRACT

The two principal objective of this research are to determine the effect of fluorine and fluorine content on the thermal and oxidative stability of polyester laminating resins; and to investigate the preparation of perfluoroglutaronitrile, perfluoroadiponitrile, the corresponding imidine and amidine, and rigid polymers derived therefrom.

Polyesters have been synthesized from fluorinated glycols and the corresponding hydrocarbon glycols. Laminates prepared from these polyesters have been aged at elevated temperatures and their physical properties measured before and after aging. In general, the fluorinated polyester laminates exhibit much better retention of physical properties than their hydrocarbon analogs.

The report also contains a description of synthetic work directed toward the preparation of fluorine-containing compounds used in the preparation of polyesters and as cross-linking monomers.

The preparation and polymerization of perfluoroglutaronitrile is described. The polymerization of perfluoroglutarimidine and perfluoroadipamidine has been investigated.

Research on the synthesis of certain novel or unusual fluorine-containing intermediates considered desirable for polymerization in this project was performed at Purdue University under sub-contract to Hooker Chemical Corporation. Details of this work performed at Purdue during the contract year comprises Appendix I of this report.

PUBLICATION REVIEW

This report has been reviewed and is approved

FOR THE COMMANDER

A. M. Lovelace

Dr. A. M. Lovelace
Chief, Polymer Branch
Non-Metallic Materials Division
Materials Laboratory

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I. INTRODUCTION

The ultimate goal of the research being performed by the Hooker Chemical Corporation under contract with the Materials Laboratory, Wright Air Development Center, is to determine the effect of fluorine and fluorine content on the thermal and oxidative stability of unsaturated polyester laminating resins. An additional function is to aid in the investigations of the perfluorinated amidine polymers currently of interest to WADC.

The basic premises for the program currently under investigation are that esters of polyesters containing no β C-H atoms in the alcohol or glycol segment are not subject to the same pyrolytic degradation at elevated temperatures as are esters containing β C-H groups. Further, the presence of fluorine increases the oxidative stability of compounds and the degree of stability is dependent upon fluorine content and location in the molecule. The latter premise would become important both with regard to the polyester itself and the cross-linking monomer used in the preparation of the resin.

The laboratory work to date has been concerned mainly with the preparation of intermediates, establishing polymerization or esterification conditions for the fluorinated glycols and preparation of polyesters from the corresponding hydrocarbon glycols. Compounding studies of these polyesters with known high temperature cross-linking monomers have been performed and a number of glass cloth laminates prepared. Experiments were designed to standardize the impregnation and lamination procedures so that the optimum properties are obtained which will give meaningful and reproducible results. A program of aging and testing at elevated temperatures is being developed for the evaluation of these polyester resins. In addition, a portion of the program was devoted to the synthesis of new fluorine-containing acids and alcohols for use in the preparation of polyesters and unsaturated monomers.

The perfluorinated amidine polymers mentioned previously are of interest to WADC because of their thermal and oxidative stability above 400° C. By variation of proportions of perfluorinated mono- and di-amidines, polymers may be obtained which range from fluids to elastomers to resins. Extensive investigations of these polymers, however, has been hampered by a shortage of starting materials. The research program initiated by the Hooker Chemical Corporation has as its objective the preparation of these raw materials in sufficient quantities to allow other WADC contractors designated by that agency to continue investigations in the realm of perfluorinated amidine polymers and elastomers. It is further an objective to investigate the preparation of perfluoroglutaronitrile by all the

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known means of nitrile formation so that an easy, convenient method for its preparation may be developed. Effort has been expended to develop methods of polymerizing perfluoroglutaronitrile, perfluoroglutarimidine and perfluoroadipamidine. Particular emphasis is being placed on determining suitable conditions under which these materials may be molded to give rigid materials which might have unusual thermal stability.

Research on the synthesis of fluorine-containing intermediates considered desirable for polymerization in this project has been performed at Purdue Research Foundation under sub-contract to Hooker Chemical Corporation. Details of the synthetic work performed at Purdue during the contract year is contained in the Appendix of this report. The following is a list of work done at Purdue.

1. The reaction of iodoheptafluoropropane with allyl bromide under U.V. light yielded a compound believed to be tetradecafluorohexane.

2. The yield of 1,7-diiodo-3,3,4,4,5,5-hexafluoroheptane was increased to 87%.

3. 1,6-Diodo-3,3,4,4-tetrafluorohexane was prepared.

4. Attempts at preparing the Grignard reagent from 1,7-diiodohexafluoroheptane were unsuccessful.

5. 3,3,4,4,5,5-Hexafluoroheptane-1,7-diol diacetate was prepared.

6. 3,3,4,4,5,5-Hexafluoroheptane-1,7-diol was prepared.

7. 3,4,4,5-Tetrafluorohepta-2,5-diene-1,7-dicarboxylic acid was prepared.

8. 3,3,4,4,5,5-Hexafluoropimelic acid was prepared.

9. A product from the reaction of 1,7-diiodohexafluoroheptane with potassium cyanide is under investigation.

10. The following attempted reactions under various conditions, were unsuccessful:

    Tetrafluoroethylene with butyne-1,4-diol diacetate; with 2,3-dichloro-1,1,1,4,4,4-hexafluorobutene-2; with ethyl γ,γ,γ-trifluorocrotonate; with furan.

    Hexafluoropropene with allyl alcohol; with allyl chloride; with acrylonitrile; with furan.

    Hexafluorobutadiene with allyl alcohol; with sulfur dioxide.

11. The reaction of hexafluorobutadiene with methanol under free radical conditions gave a solid which is under investigation.

12. 2,3-Dichloro-1,1,1,4,4,4-hexafluorobutene-2 with cuprous chloride was unsuccessful.

13. An attempt at dechlorinating 2,3-dichlorohexafluorobutene-2 with cuprous chloride was unsuccessful.

14. Ethyl 2,3-dibromo-4,4,5,5,6,6,6-heptafluorohexanoate was prepared.

15. Ethyl 2,3-dibromo-4,4,4-trifluorobutyrate was prepared.

16. Propiolic acid and its ethyl ester were prepared.

17. The reaction of ethyl propiolate with trifluoropropyl iodide gave a product which is under investigation.

18. 1-Bromo-3,3,3-trifluoropropene was prepared.

19. Acetylene dicarboxylic acid and its ethyl acid ester were prepared.

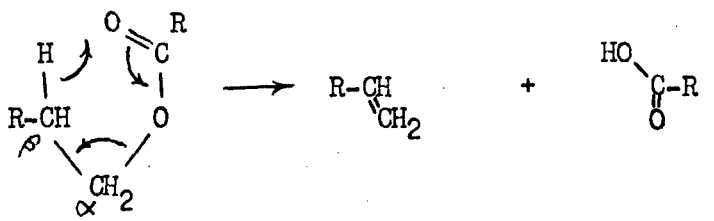
20. 2,5-bis(Trifluoromethyl)benzoic acid was prepared.

21. The reaction of pyromellitic acid with sulfur tetrafluoride gave a product believed to be bis(trifluoromethyl)phthalic anhydride.

II. DISCUSSION

A. Fluorine-Containing Unsaturated Polyester Resins

The purpose of this investigation is to determine the effect of fluorine in polyester laminating resins. Since the fluorinated glycols, such as 2,2,3,3,4,4-hexafluoropentanediol-1,5 (HFPD), have no hydrogen atoms attached to the β carbon atoms; it was felt that the polyesters made from these glycols would not be subject to the same pyrolytic degradation that is the fate of their hydrocarbon analogs. The usual mechanism of pyrolysis of esters may be shown as follows:



Further, it was felt that the fluorine-containing polyesters would exhibit increased oxidative stability and that the degree of stability would be dependent on the amount of fluorine and its position in the molecule.

Since there are so many variables contributing to the overall composition of a polyester resin laminate, any attempt to establish the effect of a change in the molecular structure of any of the components must of necessity be done on a comparative basis. Our program has been mainly concerned with substitution of fluorine for hydrogen in the glycol portion of the polyester and the effect of this substitution on the high temperature aging characteristics of the derived laminates. The methods of polyester synthesis and the laminating procedures have been previously described.[1]

The laminates prepared during this report period are listed in Tables I through VI. Table I lists laminates prepared from fluorinated and hydrocarbon glycol polyesters and various cross-linking monomers. The table is arranged with the hydrocarbon glycol polyester laminates first, followed by the fluorinated polyester laminates. Both are arranged by chain length of the glycol. It was found that the fluorinated polyester resin laminates had a higher retention of room temperature flexural strength after 100 hours at 260°C (500°F) than did the corresponding hydrocarbon glycol polyester laminates. The fluorinated glycol polyester laminates lose only 25-38% of their initial flexural strength after the indicated aging while the hydrocarbon analogs lose 66-75% of their initial flexural strengths after aging at the same temperature for the same period of time. These results were

obtained when the laminates were prepared with triallyl cyanurate, diallyl isophthalate or diallyl terephthalate as the cross-linking monomer. Figure 1 presents data on fluorinated and hydrocarbon glycol polyester laminates made with triallyl cyanurate monomer. Figure 2 gives similar data for laminates cross-linked with maleimide and with maleimide-triallyl cyanurate mixtures. It is obvious that maleimide is a superior high temperature monomer.

When a mixture of maleimide and triallyl cyanurate is used as the cross-linking monomer the difference in the high temperature properties between the fluorinated and hydrocarbon glycol polyester laminates is considerably reduced (see laminates 92A-97A and 100A, Figure 2). It seemed desirable to prepare laminates from the monomers only to determine how much the polyesters contribute to the laminates (see 109A and 110A and of Table I). It is apparent that the polyesters do add strength to the laminates.

Table II lists a series of laminates prepared with various polyester-monomer ratios. The differences are not profound, but it does appear that ratios approximating 1:1 are optimal.

The acid portion of the usual polyesters is three parts fumarate and one part isophthalate. The isophthalate segments are added to reduce the crystallinity and the melting points of the polyesters and thus facilitate the laminating operation. The initial flexural strengths of the fluorinated polyester laminates (except those prepared with maleimide) are rather low, 40,000 to 46,000 psi. It was hoped that by reducing the number of isophthalate segments, that a higher cross-linking density would be obtained, which would be reflected in higher initial flexural strengths. That this was not the case may be seen by inspection of Table III.

Examination of Table IV indicates that varying the concentration of the peroxide catalyst between 0.5% and 2% has a relatively minor effect on the aging characteristics of the laminates whether they are tested at room temperature or at 260°C.

In Table V and Figure 3 are included data on laminates aged at 316°C (600°F). Increasing the aging temperature 100°F, from 500°F to 600°F, produces a marked acceleration in the deterioration of the laminates. Laminate 107A, which still retains appreciable strength after 50 hours, graphically indicates the superiority of maleimide.

A program of high temperature testing of the polyester resin laminates has been begun, but only a limited amount of data is presently available. The results of these elevated temperature testing of the laminates along with other pertinent information are tabulated in Table VI. The results further confirm the improved high temperature aging characteristics of the fluorine-containing polyester resin laminates as compared to their corresponding hydrocarbon glycol polyester laminates. This may be seen in

Figure 4 where we compare the high temperature (260°C) flexural strengths after aging of a triallyl cyanurate cross-linked polyester resin prepared from HFPD (laminate 35-A, 35-B) with its corresponding pentane diol polyester resin laminate (33-A, 33-B). After 100 hours at 260°C the fluorinated polyester laminate still retains 90% of its initial high temperature strength whereas the hydrocarbon glycol polyester retains only 29% of its initial high temperature strength. A similar result was obtained when diallyl isophthalate was the cross-linking monomer. The fluorinated polyester laminate (36-A, 36-B) retains 85% of its initial elevated temperature strength after aging 100 hours at 260°C whereas the hydrocarbon glycol polyester laminate retains only 40% of its initial strength (37-A, 37-B).

The data has been extended to include polyesters prepared from the C_4 and C_6 glycols, both the hydrocarbon and fluorinated materials. No differences have been observed in the high temperature aging characteristics of the laminates which could be attributed to the chain length of the glycols.

Examination of the data of Table VI permits one to draw certain other conclusions regarding the polyester resin both with regard to the cross-linking monomer and to the polyester itself especially to the possible effect of fluorine on the thermal stability of the polyester resin laminates. In all cases, diallyl isophthalate cross-linked polyester resin laminates (34-A, 34-B, 36-A, 39-A, 40-A, 39-B, 40-B, 47-A, 48-A) are weaker than the triallyl cyanurate cross-linked polyester resin laminates. (33-A, 33-B, 35-A, 35-B, 37-A, 37-B, 38-A, 38-B, 45-A, 46-A). In addition, we have found that the diallyl isophthalate cross-linked polyester resin laminates of the hydrocarbon glycol polyesters (34-A, 34-B, 39-A, 40-A, 40-B) are undergoing further cross-linking during at least the first 25 hours of the aging process at 260°C. This effect, however, does not occur with fluorinated glycol polyesters cross-linked with diallyl isophthalate. No improvement is elevated temperature flexural strength occurred during the aging process indicating no further cross-linking occurring during the aging.

TABLE I

PREPARATION AND HEAT AGING OF POLYESTER LAMINATES

Laminate Code	Polyester	Monomer	Flex. Str. x 10^{-3} After Aging at 260°C. (Weight Losses Based on Laminates) 0 Hrs	8 Hrs	25 Hrs	50 Hrs	100 Hrs	200 Hrs
9-E	BD-FC-IPC 75:25	TAC	35.7	30.8 (6.9)	20.9 (11.4)	11.4 (13.7)	13.7 (16.9)	
25-A	BD-FC-IPC 75:25	TAC	35.2	31.0 (5.6)	24.6 (11.2)	13.8 (14.3)	11.0 (16.0)	9.1 (18.5)
21-A	BD-FC-IPC 75:25	DAIP	50.6	39.7	-	17.8	11.6	
27-A	BD-FC-IPC 75:25	DAIP	35.5	34.4 (6.6)	24.4 (18.0)	16.8 (23.2)	12.8 (26.0)	7.7 (28.0)
14-A	PD-FC-IPC 75:25	TAC	35.6	29.2 (8.1)	19.2 (12.2)	13.3 (15.0)	10.1 (17.6)	
13-A	PD-FC-IPC 75:25	TAC	35.6	33.9 (8.2)	17.4 (12.5)	12.3 (15.5)	10.6 (18.6)	
15-A	PD-FC-IPC 75:25	DAIP	42.2	34.3 (10.9)	24.0 (19.3)	17.6 (22.2)	10.6 (23.6)	
22-A	PD-FC-IPC 75:25	DAIP	49.4	39.6	-	14.9	9.2	
22-B	PD-FC-IPC 75:25	DAIP	46.9	45.9 (6.5)	32.8 (17.3)	22.3 (21.5)	13.4 (22.2)	8.0 (25.6)
24-A	PD-FC-IPC 75:25	DAN-TAC 50:50	44.5	32.0	-	14.7	9.4	
24-B	PD-FC-IPC 75:25	DAN-DAIP 50:50	47.2	41.7 (7.6)	23.4 (14.5)	12.7 (17.4)	9.9 (18.9)	6.0 (20.8)
44-A	PD-FC-IPC 75:25	DATP	35.9	36.9 (7.2)	23.6 (19.6)	16.1 (23.1)	9.5 (25.6)	
99-A*	PD-FC-IPC 75:25	TAC-MI 50:50	53.9	48.7 (3.0)	47.5 (6.0)	37.0 (8.1)	24.9 (10.3)	

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See p.18 for code.

TABLE I (CONTINUED)

PREPARATION AND HEAT AGING OF POLYESTER LAMINATES

Laminate Code	Polyester	Monomer	Flex. Str. x 10^{-3} After Aging at 260°C. (Weight Losses Based on Laminates) 0 Hrs	8 Hrs	25 Hrs	50 Hrs	100 Hrs	200 Hrs
100-A*	PD-FC-IPC 75:25	TAC-MI 25:75	68.4	65.1 (2.5)	47.0 (7.7)	43.2 (9.5)	39.6 (10.8)	
26-A	HD-FC-IPC 75:25	TAC	40.9	37.7 (6.3)	22.2 (11.4)	16.4 (14.1)	12.8 (16.6)	7.7 (19.5)
28-A	HD-FC-IPC 75:25	DAIP	50.0	43.7 (8.0)	25.5 (18.1)	18.7 (20.5)	11.9 (21.8)	
58-A	HD-FC-IPC 75:25	3FDATP	37.0	30.3	21.9	12.5	8.3	
108-A*	DFPD-FC-IPC 75:25	TAC	42.7	46.8 (4.1)	41.4 (9.5)	36.1 (17.3)	36.1 (18.0)	
31-A	TFBD-FC-IPC 75:25	TAC	30.0	-	26.2 (11.1)	24.6 (18.1)	19.2 (20.8)	
31-B	TFBD-FC-IPC 75:25	TAC	33.7	26.4 (4.7)	28.0 (9.7)	23.6 (14.4)	20.0 (18.7)	
10-A	HFPD-FC-IPC 75:25	TAC	40.1	39.6 (6.1)	35.1 (12.6)	31.8 (18.1)	27.6 (21.5)	
10-B	HFPD-FC-IPC 75:25	TAC	39.6	38.2 (6.4)	31.3 (13.5)	29.7 (17.3)	26.9 (21.8)	
16-A	HFPD-FC-IPC 75:25	DAIP	47.1	46.1 (3.1)	37.3 (11.0)	36.5 (16.2)	34.4 (20.1)	
23-B	HFPD-FC-IPC 75:25	DAIP	50.2	41.0 (3.1)	39.5 (9.7)	35.1 (15.9)	29.5 (19.6)	24.9 (23.8)
23-A	HFPD-FC-IPC 75:25	DAIP	40.5	38.6	-	31.6	26.6	
43-A	HFPD-FC-IPC 75:25	DATP	37.4	36.4 (3.0)	29.1 (11.6)	27.1 (15.8)	25.5 (20.0)	

TABLE I (CONTINUED)

PREPARATION AND HEAT AGING OF POLYESTER LAMINATES

Laminate Code	Polyester	Monomer	Flex. Str. x 10^{-3} After Aging at 260° C. (Weight Losses Based on Laminates) 0 Hrs	8 Hrs	25 Hrs	50 Hrs	100 Hrs	200 Hrs
91-A*	HFPD-FC-IPC 75:25	TAC-MI 75:25	41.3	40.0 (5.2)	33.5 (12.2)	29.0 (15.5)	26.9 (19.8)	
92-A*	HFPD-FC-IPC 75:25	TAC-MI 50:50	66.1	63.1 (3.4)	48.9 (10.1)	47.0 (12.5)	33.8 (17.3)	
97-A*	HFPD-FC-IPC 75:25	TAC-MI 50:50	57.9	53.0	45.1	47.5	40.1	
93-A*	HFPD-FC-IPC 75:25	TAC-MI 25:75	61.6	65.2 (2.0)	40.3 (6.1)	47.2 (7.9)	38.1 (13.0)	
98-A*	HFPD-FC-IPC 75:25	TAC-MI 25:75	63.8	65.0	50.8	51.1	43.2	
101-A*	HFPD-FC-IPC 75:25	MI	44.0	52.2 (2.0)	52.9 (5.1)	52.4 (7.7)	49.2 (10.6)	
106-A*	HFPD-FC-IPC 75:25	MI	62.5	-	59.1 (0.7)	63.3 (2.6)	46.3 (6.8)	
11-A	HFPD-FC-IPC 75:25	TAC-DAN 50:50	40.9	37.3 (8.6)	32.7 (15.3)	30.8 (18.6)	27.3 (22.2)	
12-A	HFPD-MA-2FHET	TAC	59.6	50.4 (6.1)	40.5 (13.3)	-	28.2 (18.4)	
29-A	OFHD-FC-IPC 75:25	TAC	31.9	-	24.9 (15.3)	20.7 (20.3)	17.5 (24.3)	
29-B	OFHD-FC-IPC 75:25	TAC	36.5	30.2 (6.3)	26.6 (12.3)	25.0 (17.1)	23.5 (21.3)	
49-A	HFPD-FC-IPC 301 Glass	TAC	41.1	38.9	27.3	28.4	20.9	
50-A	PD-FC-IPC 301 Glass	TAC	38.7	28.0	15.6	11.8	8.6	
95-A*	HFPD-FC-IPC Garan Glass	TAC	43.5	33.9 (4.5)	30.3 (10.5)	20.4 (15.2)	22.5 (19.2)	

TABLE I (CONTINUED)

PREPARATION AND HEAT AGING OF POLYESTER LAMINATES

Laminate Code	Polyester	Monomer	Flex. Str. x 10^{-3} After Aging at 260°C (Weight Losses Based on Laminates) 0 Hrs	8 Hrs	25 Hrs	50 Hrs	100 Hrs	200 Hrs
96-A*	HFPD-FC-IPC Garan Glass	TAC	45.5	42.3 (4.6)	31.2 (11.0)	27.3 (16.0)	26.9 (19.8)	
104-A*	HFPD-FC-IPC 75:25	HFPDA	31.7	28.3 (3.7)	35.8 (4.3)	30.9 (8.8)	28.2 (21.8)	
105-A*	HFPD-FC-IPC	HFPDA-MI 50:50	48.5	46.0 (2.5)	45.0 (5.6)	41.5 (9.6)	35.1 (18.0)	
109-A*	-	MI	22.1	22.5 (0.4)	26.5 (0.4)	14.8 (2.2)	14.2 (1.0)	
110-A*	-	TAC-MI 50:50	63.6	56.9 (1.2)	48.8 (3.0)	-	30.1 (7.6)	

TABLE II

PREPARATION AND HEAT AGING OF POLYESTER LAMINATES

VARIATION OF POLYESTER-MONOMER RATIO

Laminate Code	Polyester	Ratio Polyester to Monomer	Flex. Str. x 10^{-3} After Aging at 260°C. (Weight Losses Based on Laminates) 0 Hrs	8 Hrs	25 Hrs	50 Hrs	100 Hrs	200 Hrs
80-A*	HFPD-FC-IPC 75:25	TAC 75:50	45.5	39.9 (9.6)	31.9 (17.9)	30.1 (20.8)	25.5 (26.7)	
18-A	HFPD-FC-IPC 75:25	TAC 60:50	49.7	44.6 (4.8)	37.3 (10.9)	33.2 (16.3)	31.9 (20.0)	22.6 (23.2)
17-A	HFPD-FC-IPC 75:25	TAC 50:50	46.1	47.3 (5.7)	36.9 (12.3)	34.7 (15.3)	32.1 (20.6)	24.0 (30.0)
78-A*	HFPD-FC-IPC	TAC 50:100	43.4	36.3 (7.7)	30.9 (13.4)	30.6 (15.6)	23.9 (21.8)	
79-A*	HFPD-FC-IPC	TAC 50:150	38.7	37.0 (6.5)	31.1 (12.0)	26.6 (14.3)	19.1 (19.5)	
19-B	PD-FC-IPC 75:25	TAC 50:33	44.9	37.4 (6.2)	29.5 (11.3)	18.1 (14.2)	12.8 (16.5)	10.1 (19.8)
20-A	PD-FC-IPC 75:25	TAC 50:40	44.1	33.1 (6.6)	21.6 (10.3)	17.6 (13.3)	16.1 (13.6)	8.7
52-A	PD-FC-IPC 75:25	TAC 50:50	45.1	44.7	23.9	21.1	13.4	

TABLE III

PREPARATION AND HEAT AGING OF POLYESTER LAMINATES

VARIATION OF THE FUMARATE-ISOPHTHALATE RATIO

Laminate Code	Polyester	Monomer	Catalyst	Flex. Str. x 10^{-3} After Aging at 260°C (Weight Losses Based on Laminates) 0 Hrs	8 Hrs	25 Hrs	50 Hrs	100 Hrs
41-A	HFPD-FC-IPC 66:34	TAC	1% BPO 1% TBPB	41.7	-	38.1 (12.4)	33.6 (16.6)	28.0 (20.3)
42-A	HFPD-FC-IPC 66:34	DAIP	1% BPO 1% TBPB	50.9	44.2 (2.9)	34.5 (10.5)	38.0 (14.3)	32.0 (18.5)
60-A*	HFPD-FC-IPC 75:25	TAC	0.75% TBPB	46.6	44.4 (5.1)	37.0 (11.8)	34.8 (15.4)	33.5
85-A*	HFPD-FC-IPC 83:17	TAC	0.75% TBPB	34.7				
86-A*	HFPD-FC-IPC 90:10	TAC	0.75% TBPB	34.8				
89-A	HFPD-FC	TAC	1% DCP	29.0	26.8	21.9	21.5	16.2
75-A	HFPD-FC	TAC	1% TBPB	33.0				
76-A	HFPD-FC	TAC	1% DTBPO	26.2				
77-A	HFPD-FC	TAC	1% DTBPO	19.2				

TABLE IV

PREPARATION AND HEAT AGING OF POLYESTER LAMINATES

VARIATION OF CATALYST AND CONCENTRATION

Laminate Code	Polyester	Monomer	Catalyst	Temp. Tested	Flex. Str. x 10^{-3} After Aging at 260° C (Weight Losses Based on Laminate) 0 Hrs	8 Hrs	25 Hrs	50 Hrs	100 Hrs
59-A*	HFPD-FC-IPC 75:25	TAC	0.5% TBPB	RT	45.7	46.9 (5.2)	36.6 (12.4)	31.5 (16.4)	28.2
60-A*	HFPD-FC-IPC 75:25	TAC	0.75% TBPB	RT	46.6	44.4 (5.1)	37.0 (11.8)	34.8 (15.4)	33.5
61-A*	HFPD-FC-IPC 75:25	TAC	1% TBPB	RT	44.2	37.4 (5.4)	33.3 (13.7)	30.2 (14.7)	27.6
62-A*	HFPD-FC-IPC 75:25	TAC	2% TBPB	RT	43.1	40.6 (5.5)	28.0 (13.0)	32.1 (16.5)	29.0
63-A*	PD-FC-IPC 75:25	TAC	0.1% TBPB	RT	47.3	44.2 (5.6)	22.1 (11.2)	14.4 (13.5)	7.2
64-A*	PD-FC-IPC 75:25	TAC	0.5% TBPB	RT	50.8	43.2 (5.8)	28.5 (11.1)	17.4 (13.1)	9.6
65-A*	PD-FC-IPC 75:25	TAC	1% TBPB	RT	48.2	42.3 (5.5)	27.5 (10.6)	17.8 (13.0)	10.4
66-A*	PD-FC-IPC 75:25	TAC	2% TBPB	RT	46.1	39.8 (5.7)	24.4 (11.3)	15.7 (13.5)	8.4

TABLE IV (CONTINUED)

PREPARATION AND HEAT AGING OF POLYESTER LAMINATES

VARIATION OF CATALYST AND CONCENTRATION

Laminate Code	Polyester	Monomer	Catalyst	Temp. Tested	Flex. Str. x 10^{-3} After Aging at 260° C. (Weight Losses Based on Laminate) 0 Hrs	8 Hrs	25 Hrs	50 Hrs	100 Hrs
67-A*	HFPD-FC-IPC 75:25	TAC	0.5% TBPB	260° C	19.5	21.2 (6.2)	19.4 (10.9)	19.5 (15.0)	19.4 (16.2)
68-A*	HFPD-FC-IPC 75:25	TAC	0.75% TBPB	260° C	23.8	20.5 (5.3)	20.9 (11.8)	22.0 (16.5)	19.6 (19.5)
69-A*	HFPD-FC-IPC 75:25	TAC	1% TBPB	260° C	19.6	24.2 (5.1)	23.1 (12.8)	22.9 (17.1)	20.8 (20.4)
70-A*	HFPD-FC-IPC 75:25	TAC	2% TBPB	260° C	19.7	21.0 (5.4)	20.8 (13.6)	22.4 (17.1)	20.3 (21.0)
71-A*	PD-FC-IPC	TAC	0.75% TBPB	260° C	19.8	25.5 (4.7)	18.4 (8.6)	11.5 (10.7)	7.5 (12.6)
73-A*	PD-FC-IPC	TAC	2% TBPB	260° C	15.6	20.7 (4.7)	16.1 (8.9)	11.0 (11.3)	7.3 (12.8)
74-A*	PD-FC-IPC	TAC	2% TBPB	RT	45.6	38.2	24.0	20.3	12.2
51-A	HFPD-FC-IPC	TAC	2% ATC 1% BPO	RT	43.8	38.9	31.9	32.1	28.8
53-A	HFPD-FC-IPC	TAC	3% ATC 1% BPO	RT	46.3	41.8	33.4	29.5	28.3
54-A	HFPD-FC-IPC	TAC	3% ATC	RT	38.6	38.2	32.2	30.7	26.4

TABLE V

PREPARATION AND HEAT AGING OF POLYESTER LAMINATES AT 600°F

Laminate Code	Polyester	Monomer	Flex.Str. x 10^{-3} After Aging at 316°C(600°F) (Weight Losses Based on Laminates) 0 Hrs	4 Hrs	8 Hrs	25 Hrs	50 Hrs
81-A*	HFPD-FC-IPC 75:25	TAC	44.5	33.9 (15.8)	28.1 (20.3)	17.1 (26.1)	10.4 (30.4)
82-A*	HFPD-FC-IPC 75:25	TAC	-	29.8 (15.2)	25.7 (19.3)	17.5 (25.9)	7.2 (30.3)
90-A*	HFPD-FC-IPC 75:25	TAC	39.2	26.2 (16.9)	22.3 (20.6)	12.2 (25.7)	3.7 (29.6)
102-A*	HFPD-FC-IPC 75:25	TAC-MI 50:50	63.1	47.4 (14.2)	38.3 (18.5)	23.2 (24.6)	6.4 (27.3)
103-A*	HFPD-FC-IPC 75:25	TAC-MI 25:75	67.1	-	27.0 (20.7)	22.8 (27.4)	4.8 (31.0)
107-A*	HFPD-FC-IPC 75:25	MI	66.4	57.2 (5.7)	49.9 (8.8)	35.9 (17.3)	23.5 (21.4)
87-A*	PD-FC-IPC 75:25	TAC	41.9	20.7 (11.8)	15.1 (14.3)	7.3 (19.9)	3.1 (22.1)
88-A*	PD-FC-IPC 75:25	TAC	48.0	23.2 (12.0)	18.8 (15.1)	7.5 (20.0)	3.8 (24.4)
106-A*	HFPD-FC-IPC 75:25	MI	2 hrs. at 700°F 11.7				

TABLE VI

PREPARATION, HEAT AGING AND HIGH TEMPERATURE TESTING OF POLYESTER LAMINATES

Laminate Code	Polyester	Monomer	Flex.Str. x 10^{-3} R.T.	Flex. Str. at 260° C After Aging (Weight Losses Based on Laminates) 0 Hrs	8 Hrs	25 Hrs	50 Hrs	66 Hrs	100 Hrs
33-A	PD-FC-IPC 75:25	TAC	27.2	26.6 -		19.8 (10.4)		9.7 (14.8)	7.7 (15.9)
34-A	PC-FC-IPC 75:25	DAIP	37.4	17.6		21.7 (18.9)	14.4 (23.2)	11.3 (23.0)	7.2 (24.2)
35-A	HFPD-FC-IPC 75:25	TAC	41.8	27.4		27.4 (12.6)		27.8 (18.9)	24.5 (21.3)
36-A	HFPD-FC-IPC 75:25	DAIP	48.8	16.8		15.2 (10.2)	14.3 (17.4)		14.1 (20.3)
37-A	BD-FC-IPC 75:25	TAC	43.8	24.3		23.2 (11.2)	16.2 (14.9)		14.4 (16.3)
38-A	HD-FC-IPC 75:25	TAC	48.1	29.4		26.4 (11.3)	13.8 (13.7)		12.1 (16.6)
39-A	BD-FC-IPC 75:25	DAIP	47.2	13.9	13.5 (7.1)	27.1 (19.2)	22.7 (22.4)		10.8 (25.4)
40-A	HD-FC-IPC 75:25	DAIP	47.6	13.3	13.9 (8.5)	23.6 (19.3)	20.3 (21.3)		10.6 (23.1)
33-B	PD-FC-IPC	TAC	41.4	16.7 -	21.0 (7.2)	14.2 (10.9)	9.3 (14.2)		6.0 (17.3)

TABLE VI (CONTINUED)

PREPARATION, HEAT AGING AND HIGH TEMPERATURE TESTING OF POLYESTER LAMINATES

Laminate Code	Polyester	Monomer	Flex. Str. x 10^{-3} R.T.	Flex. Str. at 260°C After Aging (Weight Losses Based on Laminates) 0 Hrs	8 Hrs	25 Hrs	50 Hrs	66 Hrs	100 Hrs
35-B	HFPD-FC-IPC	TAC	38.4	19.6 -	22.2 (5.9)	21.2 (12.5)	18.4 (16.3)		19.0 (20.2)
37-B	BD-FC-IPC	TAC	28.2	11.5 -	20.5 (5.9)	14.1 (10.2)	13.8 (11.8)		6.0 (15.4)
45-A	TFBD-FC-IPC	TAC	32.8	14.5 -	20.5 (5.2)	20.1 (11.7)	19.1 (15.5)		17.7 (19.3)
38-B	HD-FC-IPC	TAC	43.3	17.9 -	27.1 (6.5)	16.5 (11.4)	10.7 (14.5)		7.2 (17.1)
46-A	OFHD-FC-IPC	TAC	42.2	17.3 -	23.4 (6.9)	22.6 (13.2)	24.9 (17.3)		21.3 (21.2)

Unless otherwise indicated panels were made with 6 plies 181 Volan A fabric.

Catalyst	Cure Schedule
2% Luperco ATC 1% tert-Butylperbenzoate	30' at 80°C (press) 60' at 120°C (oven) 60' at 175°C (oven) 60' at 200°C (oven) 60' at 260°C (oven)

Flexural tests conducted on specimen 1/2" x 3 1/2" x thickness with 1 1/4" span.

*Catalyst	Cure Schedule
0.75% tert-Butylperbenzoate (or as indicated)	30' at 120°C (press) 60' at 175°C (oven) 60' at 200°C (oven) 60' at 260°C (oven)

BD - Butanediol
PD - Pentanediol
HD - Hexanediol
DFPD - Difluoropropanediol
TFBD - Tetrafluorobutanediol
HFPD - Hexafluoropentanediol
OFHD - Octafluorohexanediol
DAN - Diallyl Nadate
TAC - Triallyl Cyanurate
DAIP - Diallyl Isophthalate
DATP - Diallyl Terephthalate
MI - Maleimide
3FDATP - Diallyl Trifluoromethyl Terephthalate
HFPDA - Hexafluoropentanediol Diacrylate
FC - Fumaryl Chloride
IPC - Isophthaloyl Chloride
MA - Maleic Anhydride
BPO - Benzoyl Peroxide
TBPB - tert-Butylperbenzoate
DCP - Dicumyl Peroxide
DTBPO - Di-tert-Butyl Peroxide

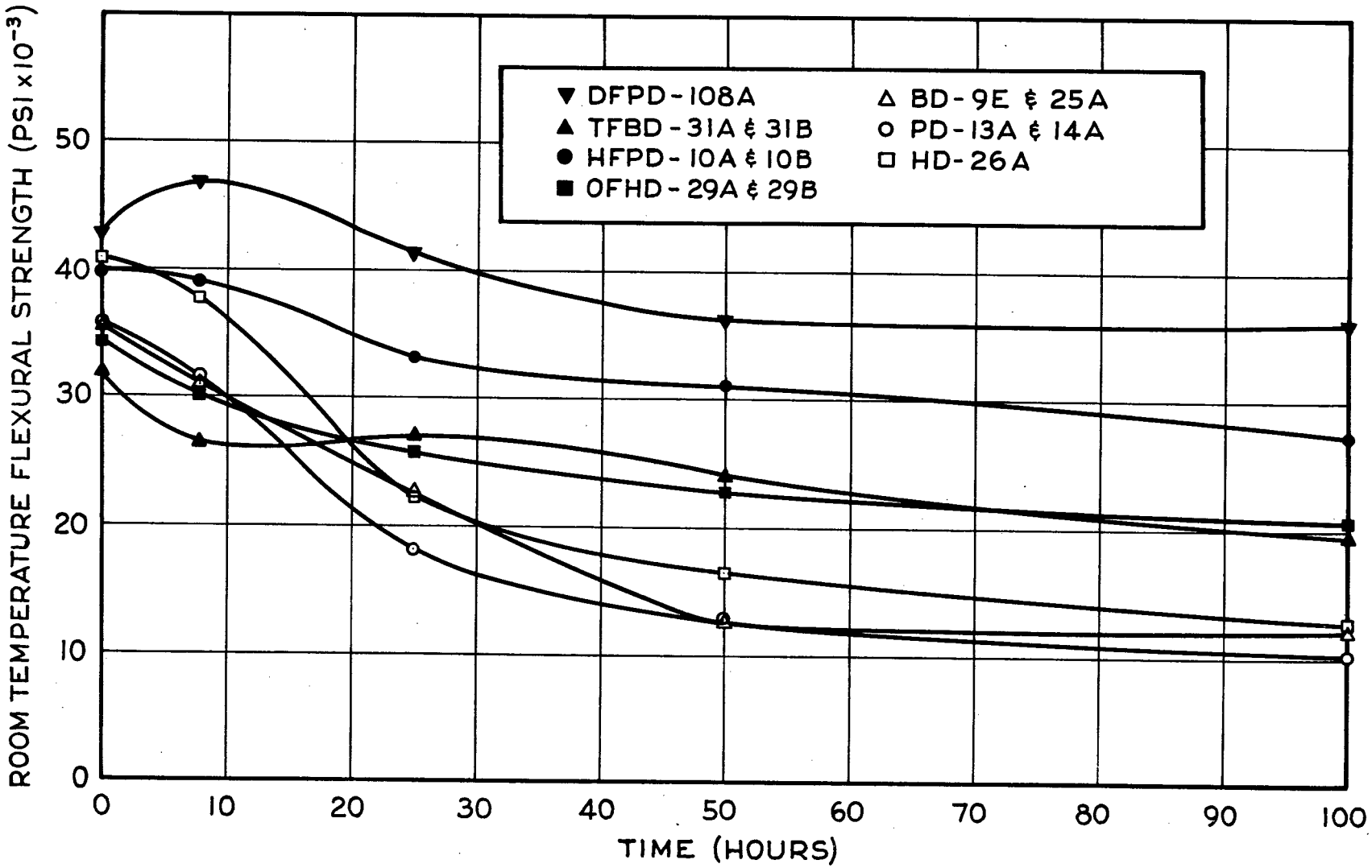


FIGURE 1

ROOM TEMPERATURE FLEXURAL STRENGTH VS. HOURS OF AGING AT 260°C. (500°F.) - TRIALLYL CYANURATE MONOMER

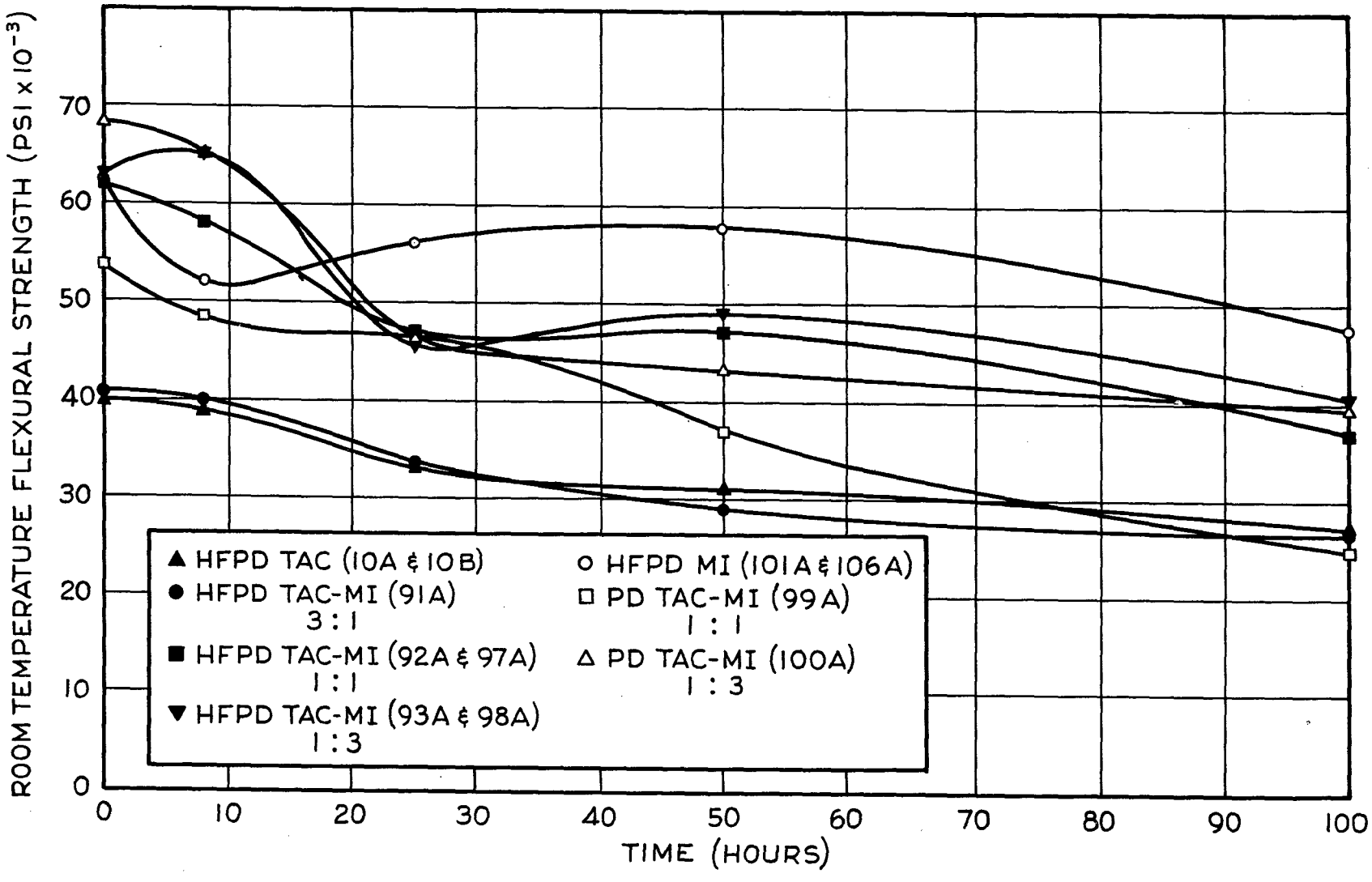


FIGURE 2

ROOM TEMPERATURE FLEXURAL STRENGTH VS. HOURS OF AGING AT 260°C. (500°F.) MALEIMIDE-TRIALLYL CYANURATE MONOMER

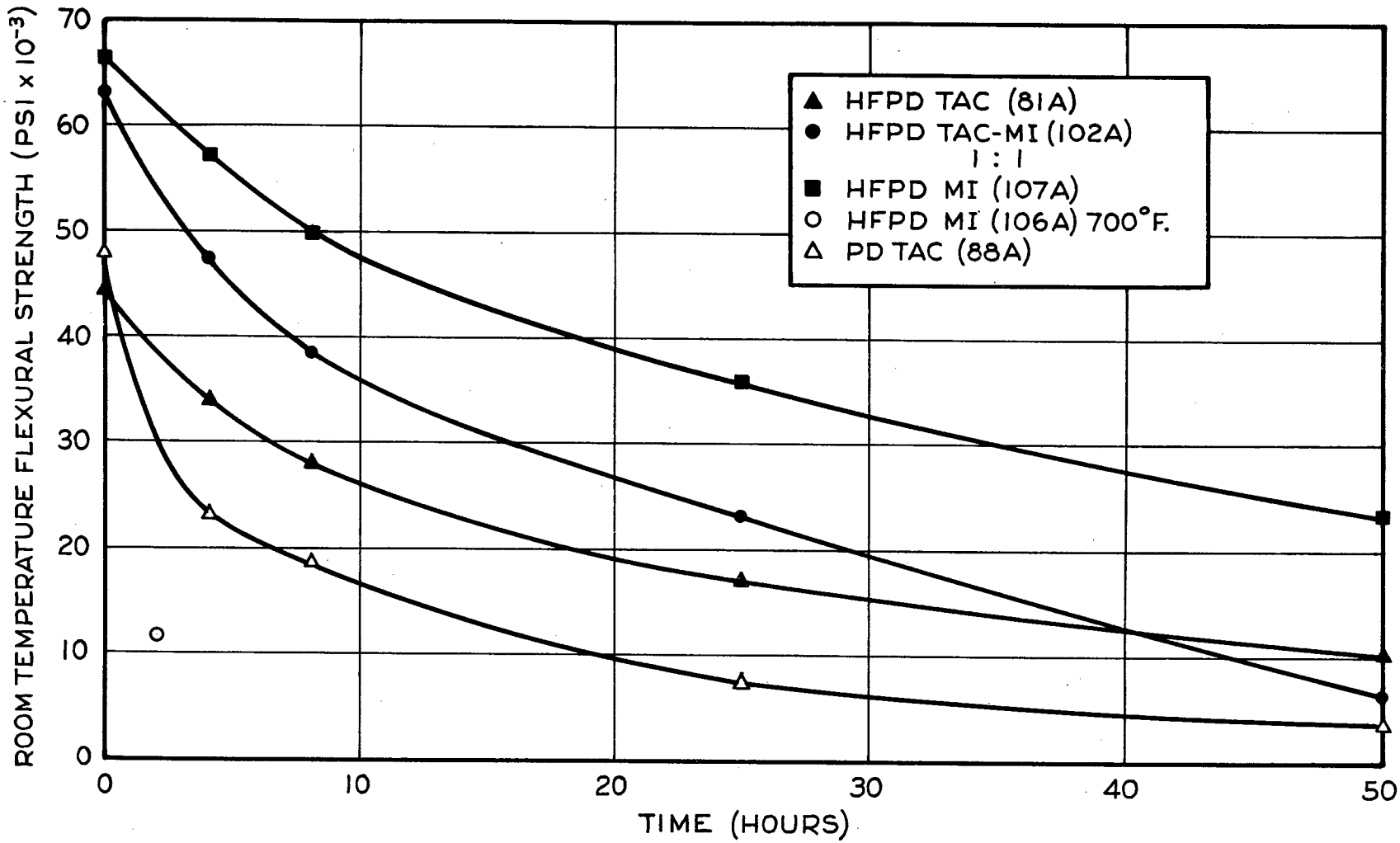


FIGURE 3
ROOM TEMPERATURE FLEXURAL STRENGTH
VS. HOURS OF AGING AT 316°C. (600°F.)

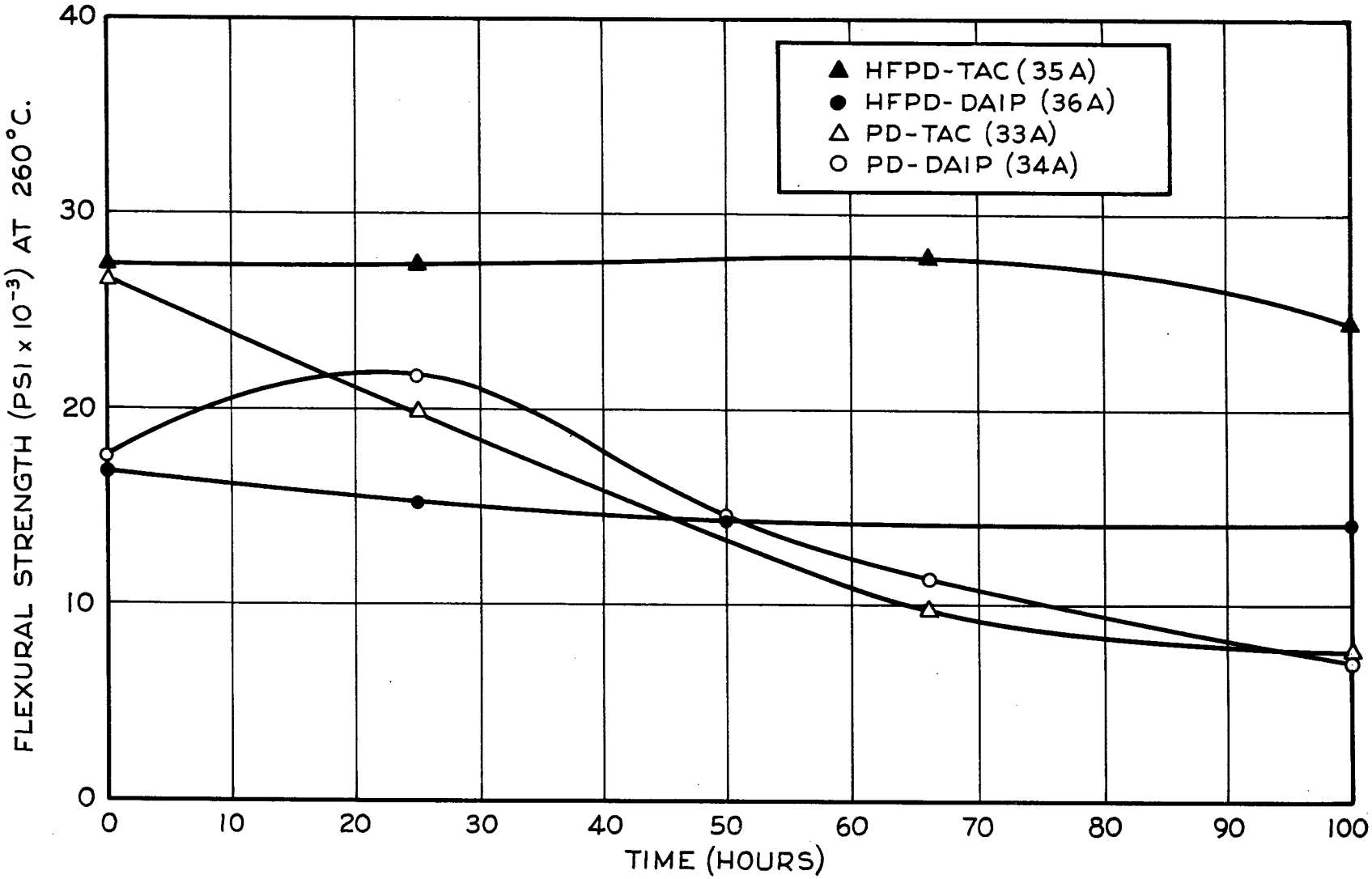
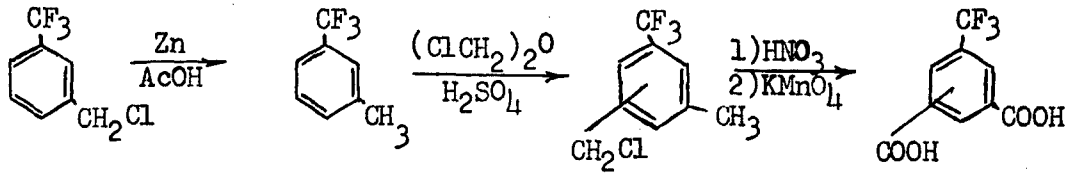


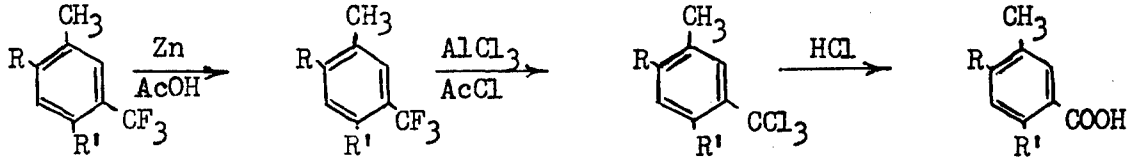
FIGURE 4
ELEVATED TEMPERATURE (260°C.) FLEXURAL STRENGTH
VS. HOURS OF AGING AT 260°C.

B. Intermediates

In the following synthetic route to the trifluoromethylphthalic acids, the chloromethylation step yields



a mixture of two isomers. These isomers cannot be cleanly separated by fractional distillation, but the early fractions are mainly "Isomer A" and the later fractions predominantly "Isomer B". Vapor phase chromatographic analysis of various fractions from the distillation indicated that fraction 3 was 82% A; fraction 8, 70% A; fraction 13, 90% B; and the reaction mixture approximately 65% A, 35% B. Isomer A was identified as 3-trifluoromethyl-4-chloromethyltoluene and Isomer B shown to be 2-chloromethyl-5-trifluoromethyltoluene by conversion to the known dimethylbenzoic acids in the following manner:

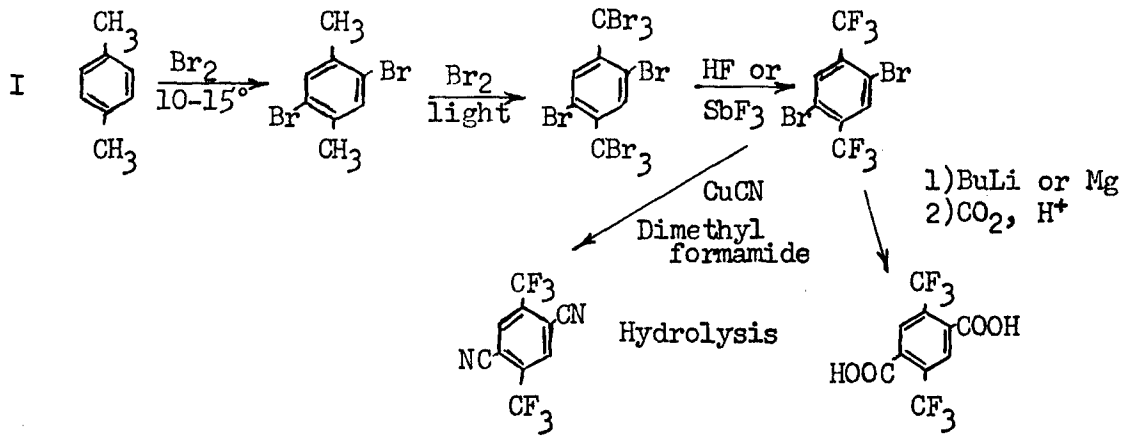


Isomer A	R=H, R'=CH_2Cl	R=H,R'=CH_3	R=H,R'=CH_3	R=H, R'=CH_3
Isomer B	R=CH_2Cl,R'=H	R=CH_3,R'=H	R=CH_3,R'=H	R=CH_3,R'=H

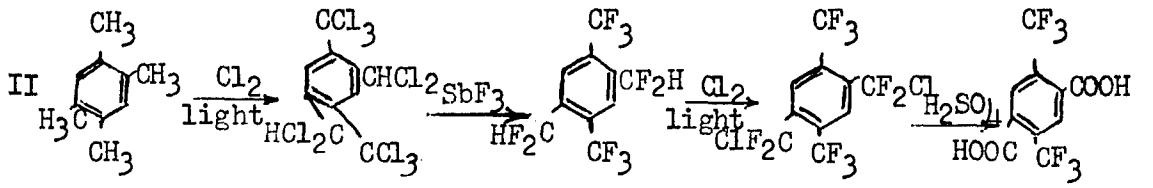
Oxidation of material rich in Isomer A yields a eutectic mixture that is 80% trifluoromethylterephthalic acid and 20% 4-trifluoromethylphthalic acid. The latter is obtained from the oxidation of Isomer B.

Diallyl trifluoromethylterephthalate (containing some diallyl 4-trifluoromethylphthalate) was prepared by the acid chloride method for use as a cross-linking monomer and found to be equivalent to diallyl terephthalate.

Some work was done on two routes directed toward the synthesis of 2,5-bis(trifluoromethyl)terephthalic acid. Reaction sequence I starting with p-xylene is as follows:

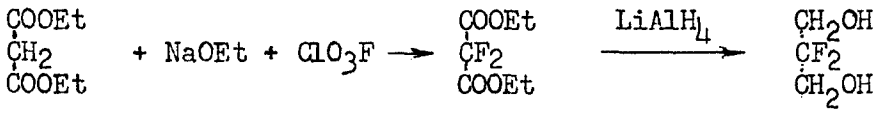


Route II, utilizing durene as starting material is represented below:

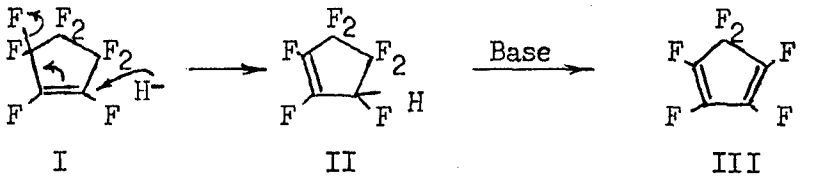


Work on the above schemes was discontinued when the elegant new method[2] of converting carboxylic acid groups to trifluoromethyl groups by means of sulfur tetrafluoride presented more attractive routes. This synthetic investigation is being continued at Purdue under subcontract (see Appendix).

Though there was little difference in the laminates prepared from 4,5 and 6 carbon fluorinated glycol polyesters, when a simple method for the preparation of the 3-carbon analog, 2,2-difluoropropanediol, became available its synthesis seemed desirable. The synthesis, made possible by Inman's[3] novel fluorination of diethyl malonate, was carried out as follows:

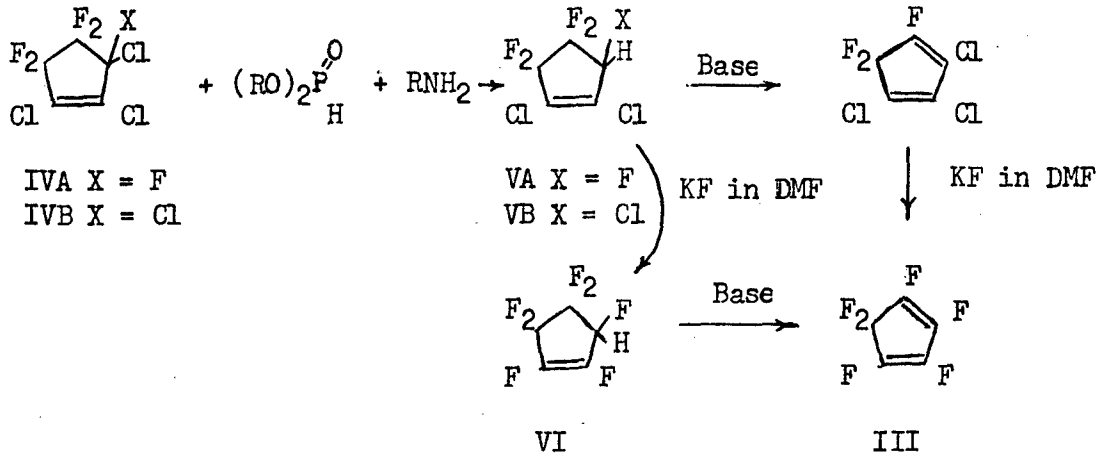


Two attempts to synthesize perfluorocyclopentadiene (III) were made. The first involved the reaction of perfluorocyclopentene (I) with lithium aluminum hydride. Miller[4] has found that many fluoroolefins react by an Sn2' mechanism. It was hoped that



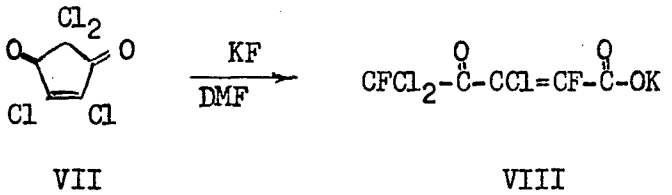
Sn2' displacement of fluoride ion by hydride ion would yield the olefin II. After the reaction was treated with water, the aqueous phase was nearly neutral (indicating that lithium aluminum hydride had reacted) and gave a strong positive test for fluoride ion.[5] The reaction gave a mixture of products that were not positively identified, but apparently the vinyl fluorine atoms were displaced as is the case in the reaction of perfluorocyclobutene with methyl lithium[6] or sodium alkoxides.[7]

The second synthetic route to perfluorocyclopentadiene involved the following reactions:



The first step hinges on the unusual reduction discovered by Atherton and Todd[8]. Certain polychloro and chlorofluoro compounds react with secondary phosphite esters in the presence of amines, the products being the reduced chloro compound, a phosphonamide and the amine hydrochloride. 1,2,3-trichloro-3,4,4,5,5-pentafluorocyclopentene (IVA) failed to react with dibutyl or diphenyl phosphite in the presence of t-butylamine, but 1,2,3,3-tetrachloro-4,4,5,5-tetrafluorocyclopentene (IVB) reacted smoothly to yield 1,2,3-trichloro-4,4,5,5-tetrafluorocyclopentene (VB). Since the trichloropentafluorocyclopentene (IVA) is converted to perfluorocyclopentene by potassium fluoride in dimethyl formamide, the conversion of VB to VI seems reasonable.

In an attempt to synthesize diethyl difluoromaleate, diethyl dichloromaleate was treated with potassium fluoride in dimethyl formamide.[9] The product appears to be diethyl chlorofluoromaleate. A similar fluorination of 1,2,4,4-tetrachlorocyclopentene-3,5-dione (VII) caused ring opening to yield VIII.



C. Perfluorinated Nitriles and Amidines

As has been noted earlier, perfluorinated monoamidines and diamidines or imidines are of great interest to the military because they can be polymerized to give polymers with relatively high thermal stability. However, a problem in this line of work is the fact that in the preparation of perfluoroglutaronitrile, a potentially available intermediate for the synthesis of perfluoroglutarimidine, yields in the dehydration of the precursor perfluoroglutaramide have generally not exceeded 60%. Thus, it would appear desirable to expend some effort in trying to improve the yield in this step.

Much work has already been carried out here and in other laboratories[10] to investigate the possible use of a variety of dehydrating agents for the conversion of perfluoroglutarimide to perfluoroglutaronitrile. However, most of the usual dehydrating agents yield very little, if any, of the nitrile. One of the more widely investigated reagents has been phosphorus pentoxide, but the highest yield of dinitrile obtained by using this material was less than 42%.

The most promising dehydrating agent found for this reaction to date has been benzotrichloride[1]. Investigations involving this reagent have already been reported[1] and show that yields of up to 60% of nitrile can be obtained. However, it was considered desirable to spend additional time on this reaction in an effort to improve the yield still further or to make the reaction more convenient to carry out.

Use of benzotrichloride alone, without the trichlorobenzene usually used as a solvent for the reaction and as a slurrying agent for the diamide, gave a 45% yield of the nitrile. An attempt to add the diamide to the reaction mixture as a solution in pyridine failed to give any nitrile. In another case, all of the reactants were mixed in the reaction vessel and heated. This removed the annoying necessity of adding the trichlorobenzene slurry of the diamide to the reaction mixture. However, only a very poor yield (15%) of the dinitrile was obtained. A number of other runs were carried out using only minor variations in the reaction conditions (temperature 175-195°, addition of the amide as a slurry in trichlorobenzene). However, good yields of the dinitrile could be obtained only when special efforts were made to keep the reaction temperature at 205-210° and to make certain that the perfluoroglutaramide was in a very fine powder when it was slurried with trichlorobenzene for addition to the reaction mixture. These yields could be duplicated even on a scale large enough to give almost one mole of perfluoroglutaronitrile in a single run.

A single experiment was carried out to investigate the use of a more reactive agent such as benzodichlorobromide as the dehydrating agent. However, most probably because the trihalide was crude and contaminated with some dibromide, bromine was given off in the reaction and this made isolation of any dinitrile difficult so that further investigations along this line were discontinued.

Several attempts to dehydrate perfluoroglutaramide by using sulfuric acid varying in strength from 100% sulfuric acid to 20% fuming sulfuric acid failed to yield the dinitrile.

Perfluoroadiponitrile was also prepared by the benzotrichloride dehydration of the corresponding diamide. Conversion of the dinitriles to the corresponding amidine or imidine generally proceeded smoothly to give a colorless product although a pale yellow product with a lower melting point was obtained in several experiments.

In order to have a better background to prepare moldings of the polymer from perfluoroglutarimidine, a study was made of the rate of evolution of ammonia during the polymerization of the imidine. Numerous runs were made in perfecting the procedure used in this study and a number of changes were made in the apparatus used. The final setup used consisted of a test tube which had a piece of glass tubing fused on near the bottom for use in the introduction of nitrogen used to flush the system. The top of the test tube was closed by means of a two-holed rubber stopper holding a thermometer and a piece of glass tubing which led to a manifold made from capillary tubing. At each arm of the manifold was placed a flask containing a known excess amount of hydrochloric acid. The reaction bath was heated to the desired temperature by a preheated oil bath which could be raised or lowered as necessary by means of a lab jack.

Generally, a known amount of the imidine was added to the preheated reaction apparatus and the apparatus was immediately closed. Zero time was then taken as the time at which the imidine was completely melted. Known excesses of hydrochloric acid were placed in flasks under each arm of the manifold and the nitrogen stream carrying the ammonia was bubbled through a solution for a predetermined length of time which depended on the stage of the reaction. The actual amount of ammonia given off during a particular time interval was then determined by titration of the excess acid with 0.1N sodium hydroxide solution to the methyl red end point. It was hoped that using the procedure and apparatus described above would keep to a minimum any time lag between the evolution of ammonia from the polymerization and the absorption of the ammonia in the hydrochloric acid.

A general idea of the data obtained in the study may be obtained from Figure 5. This plots the total amount of ammonia evolved versus time at 175° and 200°. When perfluoroglutarimidine which had been allowed to stand for several days was used in the study, a maximum of about 85% of the theoretical amount of ammonia was obtained from the polymerization. However, if the imidine was freshly prepared and allowed to stand under an aspirator to remove traces of excess ammonia used in the preparation, then almost 99% of the theoretical amount of ammonia was obtained. This does not take into account the possibility that a small amount of perfluoroglutarodiamidine is present with the perfluoroglutarimidine[10]. Gelation of the polymer usually occurred when about 29% of the theoretical amount of ammonia had been evolved.

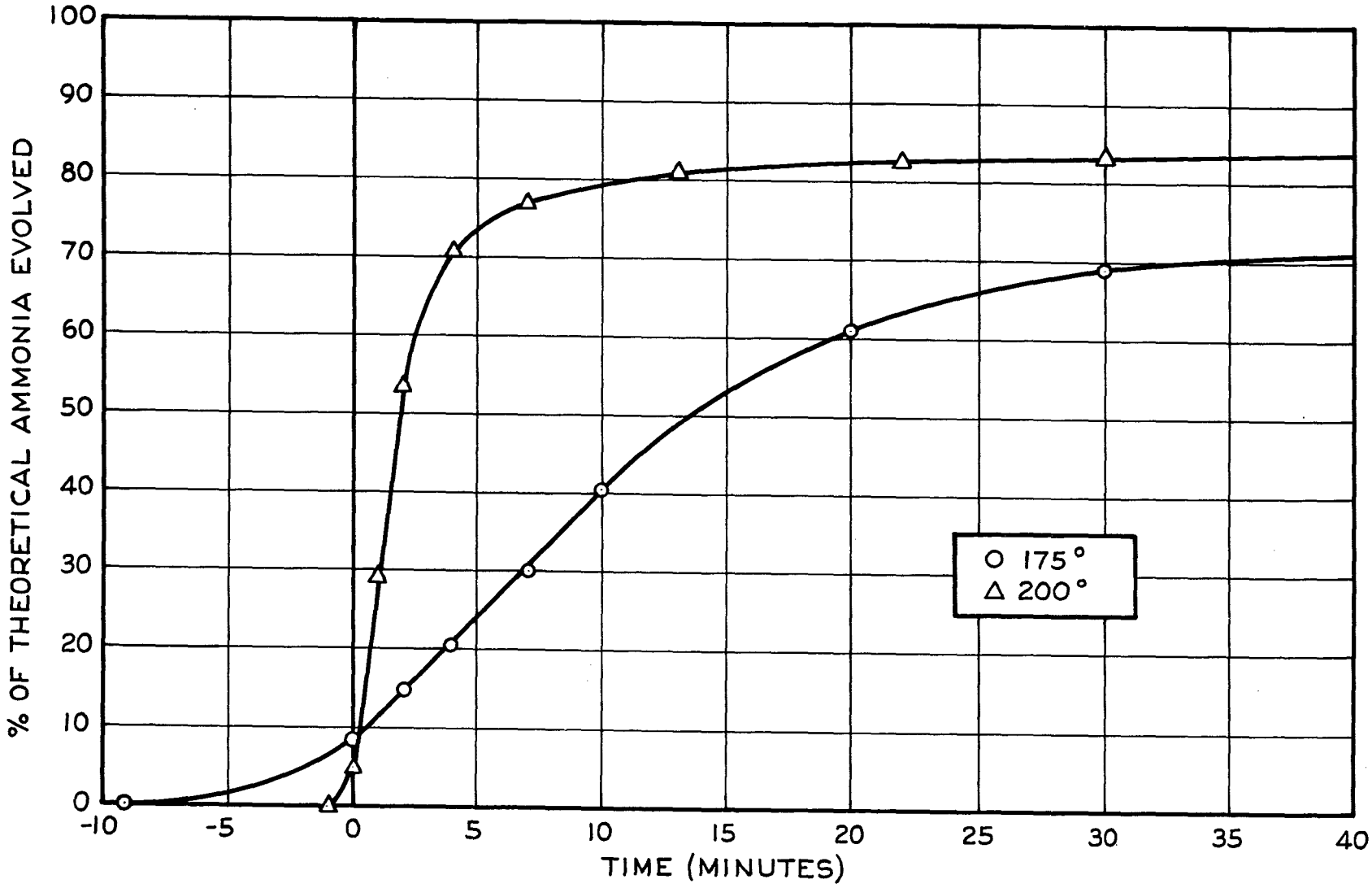
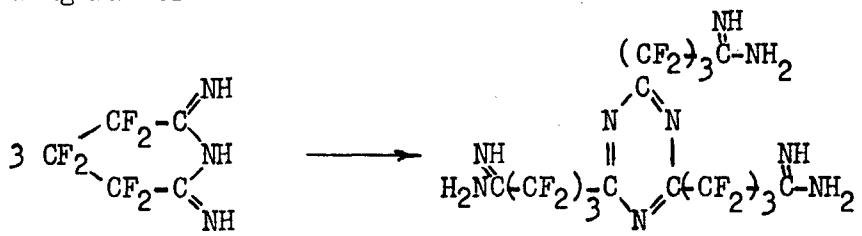
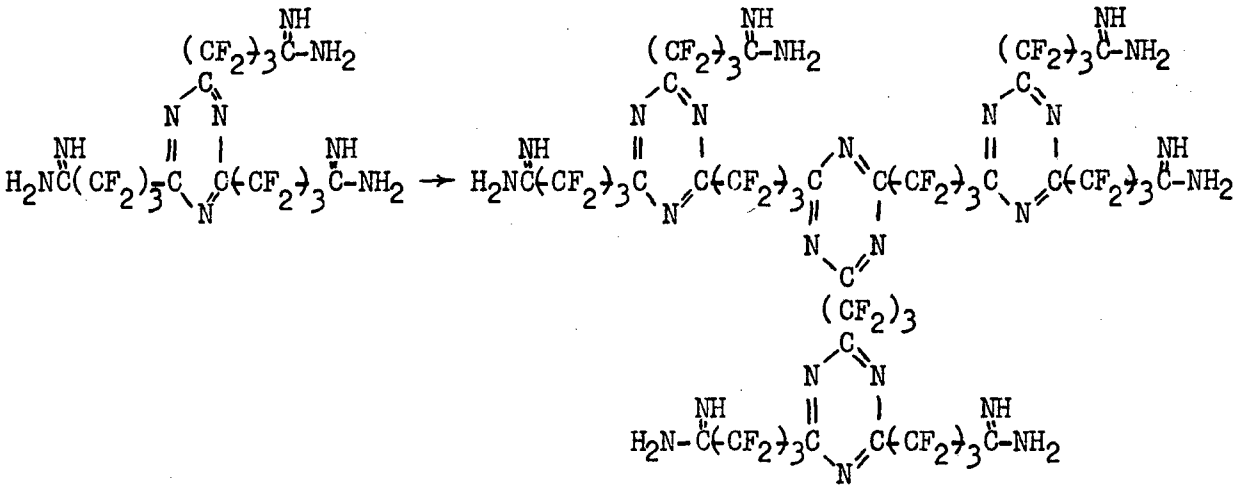


FIGURE 5
RATE OF AMMONIA EVOLUTION
IN PERFLUOROGLUTARIMIDINE POLYMERIZATION

Some consideration of the mechanism of the polymerization of perfluoroglutarimidine seems desirable at this point. The most reasonable first step would appear to be a trimerization of the imidine in the following manner:

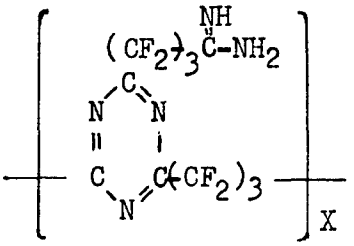


Actually, this trimerization would have to take place without the loss of ammonia. This is in contrast to the diamidines such as perfluoroadipodiamidine where it would be necessary for three molecules of the diamidine to lose three moles of ammonia in order to form the trimer. In the next step, three molecules of the trimer would then combine with loss of three moles of ammonia.



This intermediate, of course, could then react at any one of the six amidine centers to ultimately give the highly cross-linked polymer containing triazine rings connected by perfluoroalkyl groups.

As far as a correlation between the extent of cross-linking and the amount of ammonia evolved is concerned, the following repeating unit would exist in a theoretical linear perfluoroglutarimidine polymer:



Close examination of the above structure indicates that, empirically, it consists of two molecules of perfluoroglutarimidine which have lost one of the two possible molecules of ammonia between them. Thus, theoretically, when 50% of the possible ammonia has been given off in the polymerization reaction, a linear polymer would exist and any further evolution of ammonia would result from the formation of cross links of the above linear polymer.

Perfluoroglutaronitrile, when saturated with hydrogen chloride at dry ice temperature and then sealed in an ampoule, gave only a small amount of white solid whether it was kept at room temperature or heated at 100° for 30 hours. The solid appeared to be quite similar to the material formed in the dry ice trap in the preparation of perfluoroglutaronitrile. However, insufficient solid was obtained to permit a complete identification.

On the other hand, the addition of a small amount (0.5 to 2.0% by weight) of aluminum chloride to the dinitrile-hydrogen chloride mixture had a very favorable effect as far as promoting polymerization was concerned. By varying the amount of aluminum chloride added and the time and temperature for the reaction, materials which ranged from viscous liquids to a brittle solid were obtained. The extent of the polymerization could be followed quite easily by observing the infrared spectra of the products. With an increase in the degree of polymerization, the strength of the nitrile absorption band was reduced quite considerably with a corresponding increase in the strength of the -C=N- (unconjugated) absorption bands and finally, in the most highly polymerized products, an increase in the strength of the -C=N- (triazine) absorption band.

However, a drawback which has come up with the polymers obtained from catalytic treatment of perfluoroglutaronitrile is the fact that their stability is not comparable to that of the polymers obtained by heating perfluoroglutarimidine. In fact, for the most part, the polymers obtained begin to decompose at a temperature close to the maximum at which they had been heated in the sealed tube. The decomposition is slow, even as one raises the temperature considerably, but the gas evolution is quite evident.

Work has been started on preparing castings of the polymer from perfluoroglutarimidine in order to determine first if satisfactory samples could be prepared and secondly the strength, stability and other properties of the samples. The first difficulty encountered was the fact that a very dark product is obtained if the imidine is polymerized in the presence of iron. This would, of course, be quite unfortunate since molding operations are usually carried out in steel molds. However, it was found that chromium gives the usual light yellow-brown polymer so a chromium plated mold yielding castings 1 1/4" x 1/8" x 1/8" was used.

The first castings prepared with ASP 400 filler were quite weak because (1) much of the imidine, which sublimes readily, was lost during the molding operation leaving mostly compressed filler, (2) even if a large excess of imidine was used, the resultant casting contained a considerable number of gas pockets which obviously weakened the sample and (3) the imidine failed to thoroughly wet the filler. In order to overcome the above difficulties, it was found necessary to mix the perfluoroglutarimidine intimately with the filler, polymerize it partially in a test tube, grind the resultant prepolymer to a fine powder and then use this powder for the molding operation. In this way, it was possible to obtain satisfactory castings using either asbestos or ASP 400 for filler. Qualitatively, these castings had a strength comparable to similar castings of phenol-formaldehyde resin. Efforts are presently underway to establish these strengths on a quantitative basis.

III. EXPERIMENTAL

A. Intermediates

Chloromethylation of 3-Trifluoromethyltoluene. 3-Trifluoromethyltoluene (625 g., 3.9 moles) was chloromethylated by the procedure previously described.[1] Distillation of the product through a 4 ft., glass helices-packed column yielded 16 fractions b.p. 101-109°C at 20 mm., weighing 676 g. (83%). Vapor phase chromatography indicated that the early fractions were primarily Isomer A, subsequently shown to be 3-trifluoromethyl-4-chloromethyltoluene, and that later fractions were predominantly Isomer B, identified as 2-chloromethyl-5-trifluoromethyltoluene. Fraction 3 was 82% A; fraction 8, 70% A; and fraction 13, 90% B. The total composition was ~ 65% A and 35% B.

2-Trifluoromethyl-p-xylene. 3-Trifluoromethyl-4-chloromethyltoluene, 82% Isomer A, (20.9 g., 0.1 moles) was reduced with 25 gm. zinc dust in 100 ml. glacial acetic acid by the method of Ried and Boden[12]. The product, 9.9 g. (57%) b.p. 154-158°C., n_D^{24} 1.4410 was shown to have 81% isomer purity by VPC.

2,5-Dimethylbenzoic acid. 2-Trifluoromethyl-p-xylene was converted to 2-trichloromethyl-p-xylene by the method of Henne[13]. To a stirred solution of 2-trifluoromethyl-p-xylene (1.73 g., 0.1 moles) in 10 ml. acetyl chloride was added aluminum chloride (1.23 g., 0.093 moles) over a period of 1.5 hours at 0-15°C. After standing overnight the thick red-brown reaction mixture was poured into 100 ml. ice water; an oil separated at the bottom of the beaker. The mixture was transferred to a 250 ml. flask, 50 ml. conc. HCl was added and the mixture refluxed 4 hours. The flask was cooled and the product, white needles, collected by filtration. After one recrystallization from ethanol, 0.52 g. acid, m.p. 123-133°C., was obtained. Two further recrystallizations from aqueous ethanol yielded 2,5-dimethylbenzoic acid, m.p. 133-5°C. (Lit[14] 132°C.). The acid was converted by conventional means to the amide, m.p. 190°C (Lit[14] 186°C.); and the anilide m.p. 136° (Lit[14] 140°).

3,4-Dimethylbenzoic acid. By the same procedure described above, Isomer B was identified as 2-chloromethyl-5-trifluoromethyltoluene by reduction to 4-trifluoromethyl-o-xylene, chlorination to 4-trichloromethyl-o-xylene and hydrolysis to 3,4-dimethyl benzoic acid m.p. 167.5°-170°C. (Lit[14] 166°C.) further identified by conversion to the anilide m.p. 105-6°C. (Lit[14] 104°C.), amide m.p. 113.5-114.5°C. (Lit[14] 131°C.) and the nitrile m.p. 68-9° (Lit[14] 66°).

Trifluoromethylterephthalic acid. 3-Trifluoromethyl-4-chloromethyltoluene, 80% isomer purity, (309 g., 1.48 moles) was oxidized as reported[1] to yield 255 gm. (74%) eutectic mixture of trifluoromethylterephthalic acid (80%) and 4-trifluoromethylphthalic acid (20%), m.p. 282°C.

4-Trifluoromethylphthalic acid. 2-Chloromethyl-5-trifluoromethyltoluene, 90% isomer purity (52.5 gm., 0.25 moles) was oxidized by the same procedure used with the other isomer. From the reaction mixture was obtained 5.6 gm. (9.5%) eutectic acid m.p. 281-4°C. and 20 gm. (34%, considerable material lost in an accident) 4-trifluoromethylphthalic acid, m.p. 175°. Neutral equivalent 117; calcd. for $C_7H_3F_3$ $(COOH)_2$, 117.1.

Diallyl Trifluoromethylterephthalate. The ester, b.p. 110-120°C. at 0.4 mm., was prepared in 90% yield from the acid chloride in the usual manner. Vapor phase chromatography of the dimethyl ester prepared in similar fashion showed it to be a 77%-22% mixture of the two isomers.

2,5,α,α,α,α',α',α'-Octobromo-p-xylene. 2,5-Dibromo-p-xylene[15] was brominated according to Schindhelm[16]. The bromo compound (13.2 g., 0.05 moles) was placed in 50 ml. 3-necked flask equipped with stirrer, condenser, and dropping funnel. The flask was heated to 120°C, irradiated with a mercury vapor lamp and bromine added dropwise. A total of 54.2 gm. (0.34 moles) bromine was added over a 12-hour period at 120-190°C. The product, 24.0 g. (65%), m.p. 198-200°C, was recrystallized three times from benzene, m.p. 202-204°C. Analysis: Br = 83.5%; calcd. for $C_8H_2Br_8$, Br = 86.7%. The brominated product was hydrolyzed to 2,5-dibromoterephthalic acid, m.p. 330-332° (bubbles 318°) (Lit[14] m.p. 316-17°), neutral equivalent 164, calcd. for $C_6H_2Br_2$ $(COOH)_2$ 162.

Decachlorodurene. In a 1-liter, 3-neck flask equipped with condenser (connected to HCl trap) thermometer, gas dispersion tube, and stirrer was placed 268.4 g. (2.0 moles) durene and 2 g. benzamide. The reaction mixture was heated to 125°C., irradiated with a mercury vapor lamp, and the chlorination begun. Chlorine was introduced over a period of 26 hours while the temperature was gradually raised to 240°C. The increase in temperature was necessary to keep the reaction mixture molten, however at 240° the chlorinolysis of the methyl groups is noticeable. After chlorination the mixture was purged with nitrogen. The weight of chlorine introduced was 1487 g. (105%), the amount of HCl evolved was 792 g. (108%), and 642 g. (91%) chlorine was absorbed. After two recrystallizations from chlorobenzene, 500 g. (52%) decachlorodurene, m.p. 296°C. was obtained. An analytical sample was prepared by further recrystallization from benzene, pale yellow needles, m.p. 300-3°C. Analysis: Cl = 74.5%; calcd. for $C_{10}H_4Cl_{10}$, Cl = 74.1%.

Diethyl 2,2-Difluoromalonate. This compound was prepared in 50% yield by a slight modification of Inman's[3] procedure. Enough ethanol to ensure complete solution of the sodio diethyl malonate must be used, since the introduction of perchloryl fluoride to a suspension of sodio diethyl malonate resulted in an explosion.

2,2-Difluoropropanediol. Diethyl 2,2-difluoromalonate (27 g., 0.14 moles) was reduced with lithium aluminum hydride (8.2 g., 0.22 moles) by the method of McBee[17] to yield 10 g. (65%) 2,2-difluoropropanediol as a semi-solid. The compound separated as an oil when recrystallization was attempted from benzene or benzene-ethanol. Chromatography on alumina (activity 4) likewise yielded an oil. Two distillations yielded 7.5 g. material m.p. 54°C. (Lit[17] 52.53°C).

Fluorination of Diethyl Dichloromaleate. In a 500 ml. 3-neck flask equipped with stirrer, condenser, and thermometer was placed 17 gm. (0.29 moles) potassium fluoride and 150 ml. toluene. The potassium fluoride was dried by azeotropic distillation, and the toluene was displaced with 250 ml. dimethyl formamide. Diethyl dichloromaleate, 24.1 g. (0.1 mole) was added and the mixture heated with stirring for 16 hours at 90° followed by 8 hrs. at 110-150°C. The mixture was poured into 500 ml. ice water and extracted with ether. Distillation yielded 9.5 g. material b.p. 59-64°C. at 3 mm. The infrared spectrum has peaks at 6.05μ (CF=CCl-). Vapor phase chromatography indicates that the product is a mixture of starting material (25%) and diethyl chlorofluoromaleate (74%).

Fluorination of 1,2,4,4-Tetrachlorocyclopentene-3,5-dione with Potassium Fluoride. Tetrachlorocyclopentene-2,5-dione (23.4 g., 0.1 mole) was added to a mixture of anhydrous potassium fluoride (30 g., 0.52 moles) and 200 ml. dimethyl formamide. The mixture was stirred at room temperature for 24 hours. Half of the reaction mixture was poured into 200 ml. ice water. Extraction with ether yielded a small amount of dimethyl formamide. The aqueous phase was evaporated to dryness and the resulting solids extracted with hot chloroform-acetone solution. After decolorization with charcoal and concentration, the solution yielded 2.4 g. pale yellow needles. After two recrystallizations from chloroform-acetone, the compound decomposed at 237° (darkens 200°C.). The infrared spectrum shows no hydroxyl or normal carbonyl, but contains a broad band at 6.2-6.3μ like a carboxylate salt. The product may be $CFCl_2C{=}O$-CCl=CF-COOK resulting from ring opening. Calcd. for $C_5O_3Cl_3F_2K$: Cl = 36.4%, K = 13.4%; Found, Cl = 36.4%, K = 13.1%.

Reduction of 1,2,3,3-Tetrachloro-4,4,5,5-tetrafluorocyclopentene. In a 1-liter 3-neck flask, equipped with stirrer, condenser, and dropping funnel, were placed 139 g. (0.5 mole) 1,2,3,3-tetrachloro-4,4,5,5-tetrafluorocyclopentene, 31.5 g. (0.5 mole) t-butyl amine and 500 ml. methylene chloride. Dibutyl phosphite (97.0 g., 0.5 mole) was added dropwise with stirring and ice cooling over a period of 0.75 hr. The mixture was stirred at room temperature 2 hrs., then at reflux for 6 hrs. The mixture was filtered and the filtrate washed with water and dried. The product was distilled using water aspirator b.p. 40-60°. Redistillation at atmospheric pressure yielded 83.5 g. (68%) 1,2,3-trichloro-4,4,5,5-tetrafluorocyclopentene b.p. 137-141°C.

B. Perfluorinated Nitriles and Amidines

Perfluoroglutaramide. Perfluoroglutaramide was obtained in essentially quantitative yields by the procedure of Brown[11]. Diethylperfluoroglutarate was dissolved in ether and ammonia was condensed into the solution. The amide which precipitated was filtered with suction and washed with ether.

Perfluoroglutaronitrile and Perfluoroadiponitrile. Into a 5-liter, three-necked flask was placed 500 ml. of trichlorobenzene, 1650 ml. (2280 g., 11.6 moles) of benzotrichloride and 30 g. zinc chloride. The flask was fitted with a mechanical stirrer, vigreaux column with distilling head, thermometer and dropping funnel. The reaction mixture was heated to 205° and a slurry of 400 g. (1.68 moles) of finely powdered perfluoroglutaramide in trichlorobenzene was added over a period of 6 hours while the temperature of the mixture was maintained at 205-210°. Heating at 205-210° was continued for an additional hour. The exit gases were cooled by a spiral condenser off the distilling head and cooled in a wet ice trap followed by a series of dry ice traps. Distillation of the condensed products gave 193 g. (57.0%) of crude perfluoroglutaronitrile.

By essentially the same procedure, 50 g. (0.198 moles of octafluoroadipamide was dehydrated with benzotrichloride to give 13.5 g. (27%) of perfluoroadiponitrile.

Perfluoroglutarimidine and Perfluoroadipodiamidine. Sixty grams (0.297 moles) of distilled perfluoroglutaronitrile was placed in a 250 ml. flask equipped with a dry ice condenser and an inlet tube. Gaseous ammonia was then introduced into the system. During the first few minutes, the reaction flask was cooled intermittently in a wet ice bath to dissipate the heat given off at the start of the reaction. The introduction of ammonia was then continued until the solid which first formed was completely in solution. Then, the excess ammonia was allowed to evaporate in a stream of nitrogen leaving behind 59.0 g. (90.6%) of colorless perfluoroglutarimidine, m.p. 160-162° (Lit 160-161[11]).

The reaction of 9 g. (0.036 moles) of perfluoroadiponitrile with an excess of liquid ammonia in the same way gave 7.8 g. (81.3%) of colorless perfluoroadipodiamidine, m.p. 118-125° (Lit 125-130[11]).

IV. SUMMARY AND CONCLUSIONS

The following compounds have been prepared during the period of time covered by this report:

1. 3-Trifluoromethyl-4-chloromethyltoluene
2. 2-Chloromethyl-5-trifluoromethyltoluene
3. 4-Trifluoromethylphthalic acid
4. Trifluoromethylterephthalic acid
5. Diallyl trifluoromethylterephthalate
6. 2,5,α,α,α,α',α',α'-Octobromo-p-xylene
7. Decachlorodurene
8. Difluoropropanediol
9. Maleimide
10. Diethyl Dichloromaleate
11. Perfluorocyclopentene
12. Perfluoroglutaramide
13. Perfluoroglutaronitrile
14. Perfluoroglutarimidine
15. Perfluoroadiponitrile
16. Perfluoroadipodiamidine

When triallyl cyanurate or diallyl isophthalate was used as the cross-linking monomer it was found that the fluorinated polyester laminates had a higher retention of room temperature flexural strengths after 100 hours aging at 260°C. (500°F.) than did the corresponding hydrocarbon glycol polyester laminates. In fact, the fluorinated glycol polyester laminates lose only 25-38% of their flexural strength after the indicated aging while the hydrocarbon analogs lose 65-75% of their strength. However, when a superior cross-linking system (mixtures of triallyl cyanurate and maleimide, or the latter alone) is used the difference between the fluorinated glycol polyester laminates and their hydrocarbon counterparts is considerably reduced. A laminate prepared from a hexafluoropentanediol polyester and maleimide had room temperature flexural strengths of about 50,000 after 100 hours at 500°F. and over 23,000 after 50 hours at 600°F.

Varying the ratio of fluorinated glycol polyester to triallyl cyanurate between 75-50 and 50-150 had no profound effect on the aging characteristics of the laminates; however, ratios in the neighborhood of 50-50 appear optimal. Laminates prepared using 181 glass with Garan finish or 181-301 were slightly inferior to those prepared using Volan A. Varying the concentration of the peroxide initiator had a negligible effect on the high temperature aging properties of the laminates.

Considerable time was spent in efforts to synthesize trifluoromethylphthalic acids, bis-trifluoromethylphthalic acids, difluoropropanediol, and other interesting fluorinated intermediates. A laminate prepared using diallyl trifluoromethylterephthalate indicated that this monomer is equivalent to diallyl terephthalate.

The dehydration of perfluoroglutaramide by means of benzotrichloride to give perfluoroglutaronitrile was investigated thoroughly using a wide range of molar ratios of reactants and also a number of variations in the experimental procedure followed. The best yields of nitrile obtained were in the range 55-60%; it is encouraging that such yields could be duplicated even on a scale large enough to give almost one mole of nitrile from a single run. A small amount of perfluoroadiponitrile was also prepared by dehydration of the corresponding amide with benzotrichloride.

A quantity of perfluoroglutaronitrile was prepared and submitted to another contractor designated by WADC for preparation of perfluorinated amidines and their subsequent polymerization to elastomers.

The polymerization of perfluoroglutarimidine has been studied by following quantitatively the rate of evolution of ammonia during the process. The rate of polymerization ranges from moderate at 175° to quite rapid and almost instantaneous at 215°. Some preliminary work has been carried out on preparing moldings from the imidine monomer. This has shown that although the preparation of such samples of the imidine polymer are not as straight forward as the procedure involved in obtaining castings of phenol-formaldehyde resins, it is still possible to develop procedures for obtaining suitable samples of the imidine polymer.

Catalytic polymerization of perfluoroglutaronitrile with a combination of hydrogen chloride and aluminum chloride in a sealed tube has produced materials possessing a wide range of viscosities although they are not comparable in stability to the polymer obtained from perfluoroglutaramidine.

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VI. APPENDIX

SUB-CONTRACT WORK PERFORMED AT PURDUE UNIVERSITY

This appendix comprises the summary report of the research performed at Purdue University under sub-contract to the Hooker Chemical Corporation during the 1959 contract year.

INTRODUCTION

In the previous Annual Report on work performed on this sub-contract, the preparation of various mono- and bifunctional compounds from iodo- and diiodoperfluoropropane was described.[1] Of particular interest were α,ω-bifunctional compounds prepared by free radical addition of allyl alcohol to 1,3-diiodohexafluoropropane (Figure 6).

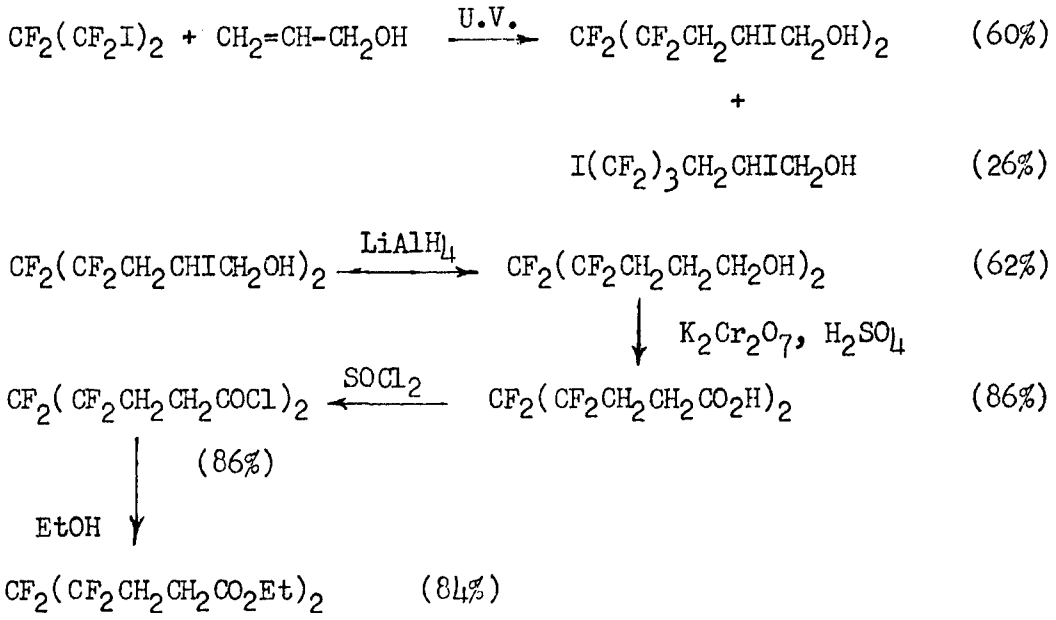

Figure 6

Although the readily available perfluorinated dibasic acid perfluoroglutaric acid undergoes polycondensation reactions, the products are subject to hydrolysis. This is ascribed to the inductive effect of the fluorine atoms which weakens, for example, the ester linkage in polyesters. The insertion of methylene units between the perfluoro cluster and the functional groups was desirable for shielding purposes. Henne and Fox, and McBee, Pierce and Smith could show a considerable decrease of the inductive effect on acids by such shielding (Table VII).[2,3]

TABLE VII

IONIZATION CONSTANTS OF ACIDS RCO_2H

R	$k_{25°}$
CH_3	$1.8\ 10^{-5}$
CF_3	$5.9\ 10^{-1}$
CF_3CH_2	$9.5\ 10^{-4}$
$CF_3CH_2CH_2$	$7.0\ 10^{-5}$

The inductive effect practically disappears upon insertion of two methylene units. Consequently, the monomers in Figure 6 are expected to be considerably resistant to hydrolysis. They are, at present, being evaluated for polycondensation purposes.

However, the presence of too many carbon-hydrogen bonds could have the adverse effect of rendering the polycondensate prone to e.g. thermal and oxidative attack. It can be seen from Table VII that the main bulk of shielding is due to one methylene unit; therefore, the preparation of less vulnerable monomers with only one methylene between the perfluoro cluster and the functional groups was undertaken. Since attempts at testing the oxidizability of unsaturates such as heptafluorohexene and hexafluorononadiene were negative,[1] another route was examined. Park et al. succeeded in condensing iodoheptafluoropropane with ethylene;[4] a preliminary analogous reaction with diiodohexafluoropropane was equally successful (Figure 2).[1]

$$CF_2(CF_2I)_2 \xrightarrow[CH_2=CH_2]{U.V.} CF_2(CF_2CH_2CH_2I)_2$$

Figure 7

The development of this reaction was considered imperative.

Another project deals with the preparation of functional fluorinated cyclobutanes. Octafluorocyclobutane is an unusually stable and inert compound; the introduction of one or two functional groups, such as hydroxyl or carboxyl, to the ring is expected to give desirable starting materials. Compounds closely resembling such entities were prepared by Hauptschein et al. who dimerized perfluoropropene to mixtures of perfluoro(dimethylcyclobutane) isomers at high temperatures and pressures.[5] The conversion of the two trifluoromethyl groups to functional groups is, however, expected to be difficult; it has not been reported.

The greater part of the work on incompletely fluorinated cyclobutanes has been reviewed by Vogel.[6] Coffman et al., in particular, synthesized many cyclic compounds from trifluoroethylene and numerous unsaturates and succeeded in obtaining functional groups on some of the products.[7]

In attempts to carry out analogous reactions with perfluoropropene, the condensation of the latter with various bifunctional acetylenes in Carius tubes was investigated.[1] However, at low temperatures no reaction occurred and at higher temperatures (150°) extensive decomposition was observed. Very small amounts of high boiling, unidentifiable, but fluorine-containing, oils were isolated.

Although Coffman's reaction between tetrafluoroethylene and acrylonitrile[7] could be reproduced, the analogous reaction with perfluoropropene yielded, next to pyrolysis products, only a small amount of fluorine- and nitrogen-containing solid.[1]

It is apparent that high temperatures are undesirable and it was felt that application of lower temperatures but higher pressures to this and similar condensation reactions should be investigated.

A third, recent, project concerns this preparation of functional aromatic compounds carrying perfluoroalkyl groups, such as phthalic acids with one or more ring hydrogens substituted by perfluoroalkyls. Three approaches were considered advisable. One is the cyclotrimerization of acetylenes carrying functional and/or perfluoroalkyl groups. Examples are (Figure 8):

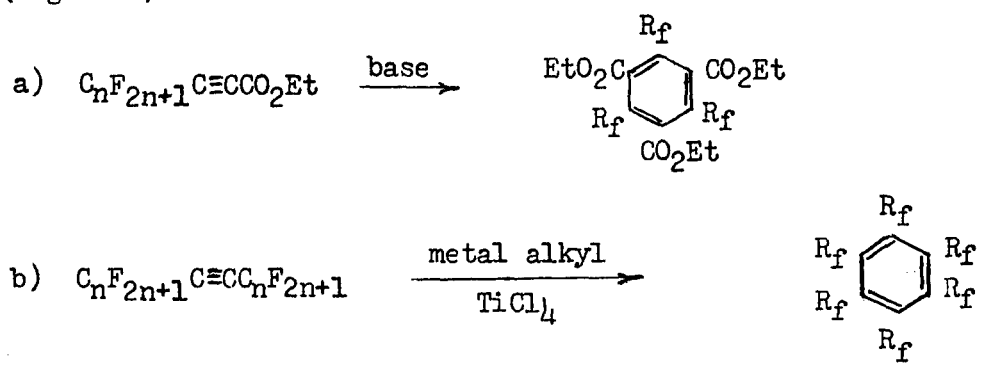

Figure 8

Not only is this last compound of great interest because of its expected considerable thermal stability, but also because of possible partial hydrolysis with concentrated sulfuric acid of one or more perfluoroalkyl to carboxyl groups.

Another approach envisages the metallation, with subsequent carboxylation, of known mono-, di- and polyperfluoroalkylbenzenes. Example (Figure 9):

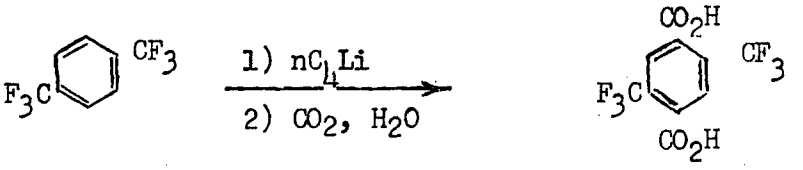

Figure 9

A third approach considers the use of the now available sulfur tetrafluoride, known to convert functional groups, such as carboxyl, to fluorocarbon groups, such as trifluoromethyl. An example of such a reaction, for our purposes, would be the conversion of pyromellitic acid to bis-(trifluoromethyl)phthalic acids.

RESULTS AND DISCUSSION

(Including Proposed Work)

α,ω-Bifunctional Fluorohydrocarbons

Although attempts at oxidizing heptafluorohexene and hexafluorononadiene by permanganate and chromic acid methods failed,[1] it was considered advisable to attempt the use of ozone as oxidizing agent. The approach was abandoned when the preparation of an intermediate, the adduct between heptafluoropropyl iodide and allyl bromide was unsuccessful. The reaction should be noted, however, since the main product, isolated in good yield, appeared to be the dimer of the heptafluoropropyl free radical, C_6F_{14}.

A more successful way of preparing the desired β,β,β',β'-tetrahydroperfluorodicarboxylic acids was seen in the following (Figure 10):

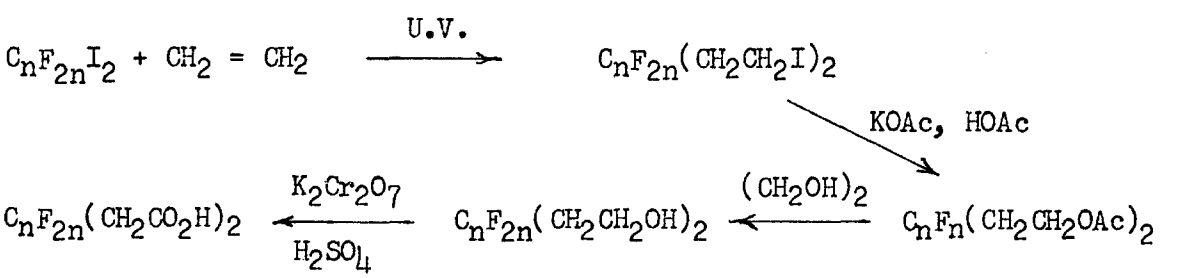

Figure 10

A preliminary reaction of 1,3-diiodohexafluoropropane with ethylene in a Carius tube, with U.V. light catalysis, was mentioned in the previous Annual Report[1]. The reaction has now been show to be reproducible and yields of up to 87% can be realized. Equally successful is the addition of two molecules of ethylene to 1,2-diiodotetrafluoroethane. An attempt at adding ethylene to diiodoperfluoropropane in the autoclave at 120°, with peroxide catalysis, failed; the diiodide was recovered. The reaction will be repeated.

The subsequent steps in the synthesis of the desired dibasic acid were carried out, according to Figure 10, with 1,7-diiodo-3,3,4,4,5,5-hexafluoroheptane. Hexafluoroheptane-1,7-diol diacetate was obtained in 56% yield. Transesterification yielded the diol almost quantitatively. The final oxidation reaction is sensitive to temperature: under vigorous conditions, chromic acid converts the diol to the unsaturated acid $CF_2(CF{=}CH{-}CO_2H)_2$. This compound was obtained in 40% yield. Dehydrofluorination thus appears to take place quite readily under acidic conditions. Although the product was not the desired one, it is considered to be of interest; for instance, polyacrylate type reactions should be investigated therewith. The desired saturated diacid was obtained in 54% yield when milder conditions were employed. The overall yield is good when compared with similar type reactions.[1]

An alternate way to the diol or diacid was attempted in the Grignardization of diiodohexafluoroheptane, with subsequent oxidation, or carboxylation, followed by hydrolysis. Remarkably, the organometallic could not be prepared, even at higher temperatures in tetrahydrofuran solvent. This is in contrast to the ease of Grignard formation with the monofunctional heptafluoropentyl iodide.[4] Should the planned experiments, U.V. irradiation for catalysis, or exchange reaction with methyllithium or phenylmagnesium halide, be equally unsuccessful, the phenomenon would merit closer inspection.

In view of the good yields in which diiodohexafluoroheptane is obtained, the conversion to the dicyano derivative is being attempted. Hydrolysis of the dicyanide would give the dibasic acid carrying two methylene units between the fluorine cluster and the functional groups. The product could thus be obtained more easily than previously described[1] (Figure 6). However, one experiment wherein $CF_2(CF_2CH_2CH_2I)_2$ was reacted with potassium cyanide in an acetone-water solution[8] did not give the desired compound, but another product which at present is under investigation. The reaction will be repeated under modified conditions.

Functional Fluorinated Cyclobutanes

The unsuitability of functional acetylenic compounds for condensation reactions with fluoroolefins was demonstrated when tetrafluoroethylene, usually a good condensing agent,[6,7] failed to react at 170° under autogenous pressure. This renders the unsuccessful experiments with the less reactive hexafluoropropene, previously reported,[1] plausible.

Perfluoropropene, however, is also unreactive at higher pressures in the autoclave. With allyl alcohol at 190° and 300 psi starting material was recovered next to small amounts of unidentifiable oils. With allyl chloride at 150°, no reaction occurred; at 180° and 1000 psi, starting material and decomposition product (tar) were obtained. Increase of pressure to 1500 psi at 150° with acrylonitrile resulted in extensive decomposition. Equally extensive decomposition was observed with 1,1,2-trichloro-3,3,3-trifluoropropene and allyl alcohol at 280° and 1700 psi. It is apparent that reactions can be obtained but that control is difficult and decomposition occurs readily. Possibly, application of very high pressures, such as 6000 psi, as employed by Hauptschein et al. for the cyclodimerization of perfluoropropene,[5] but much lower temperatures, say 50-80°, may prove successful. However, such reactions require special apparatus which, at present, are not available.

Since olefins with less vulnerable functions can be expected to decompose less easily than the carboxylated or hydroxylated analogs, one experiment was carried out with 2,3-dichloro-1,1,1,4,4,4-hexafluorobutene-2 and tetrafluoroethylene at 180° and 125 psi. It would be possible to convert the product, with two chlorine atoms, to a bifunctional compound. However, starting material was recovered. This can be ascribed to steric protection of the butene double bond by the trifluoromethyl and chlorine groups. On the other hand, the experiment with tetrafluoroethylene and the less hindered ethyl γ,γ,γ-trifluorocrotonate, known to be exceedingly reactive toward many reagents, proved equally unsuccessful in a Carius tube at 160°. Grindahl could show recently that cyclopentene reacts with perfluoropropene at 300° and 2000 psi.[9] It is proposed to react perfluoroethylene and -propene under these conditions, as final attempts in the field, with the stable 1,1,1,4,4,4-hexafluorobutyne. The expected product, a cyclobutene, could be derivatized by chlorination, with subsequent substitution of chlorine by groups such as hydroxyl or carboxyl.

Cyclopentadiene reacts very readily with both perfluoroethylene and -propene.[6] It was hoped that furan would show the same reactivity; however, the reaction of tetrafluoroethylene with furan in a Carius tube at 150° yielded starting material and only a very small amount of an unidentifiable liquid residue. The analogous reaction with hexafluoropropene at 180° gave decomposition and brittle polymerization products.

Since both perfluoroethylene and -propene proved unsuitable for these reactions, it was hoped that a diene, such as hexafluorobutadiene, would be more reactive. But, as before, the results were negative. Perfluorobutadiene gave with acrylic acid in a Carius tube at 150° only a small amount of an unidentifiable polymeric solid. With sulfur dioxide, which yields a cyclic sulfone with butadiene,[10,11] both at room temperature and at 190° in Carius tubes, only small amounts of unidentifiable oils were obtained.

One experiment of a different nature was carried out with perfluorobutadiene and methanol under free radical conditions. The analogous reaction with monounsaturated fluoroolefins is reported to give the adducts,[12] for instance (Figure 11):

$$CF_3\text{-}CF{=}CF_2 + CH_3OH \xrightarrow{\text{peroxide}} CF_3\text{-}CFH\text{-}CF_2\text{-}CH_2OH$$

Figure 11

With perfluorobutadiene, a bifunctional compound (Figure 12), possibly as precursor to dehydrofluorination products, was expected.

$$HOCH_2\text{-}CF_2\text{-}CFH\text{-}CFH\text{-}CF_2\text{-}CH_2OH$$

Figure 12

The reaction yielded a brown, impure solid; it is under further investigation.

Functional Benzenes with Perfluoroalkyl Substituents

The importance of, for instance, phthalic acids in the chemistry of polycondensation products needs no stressing, and substitution of ring hydrogen atoms by fluorocarbon radicals is an obvious tool for increasing the stability of both monomers and polycondensates. As mentioned in the Introduction, three ways are envisaged for the preparation of benzenes with one or more, preferably two, functional groups and one or more perfluoroalkyl substituents on the aromatic ring.

The first route is the cyclotrimerization of two types of acetylenes, pictured in Figure 8, a and b. Compounds type $C_nF_{2n+1}\text{-}C{\equiv}C\text{-}CO_2Et$ can be prepared in the following ways (Figure 13):

1. $C_nF_{2n+1}\text{-}CH{=}CH\text{-}CO_2Et \xrightarrow{Br_2} C_nF_{2n+1}\text{-}CHBr\text{-}CHBr\text{-}CO_2Et$[13]

$$\xrightarrow{-HBr} C_nF_{2n+1}\text{-}C{\equiv}C\text{-}CO_2Et$$

2. $HO_2C\text{-}C{\equiv}C\text{-}CO_2Et \xrightarrow[120^\circ]{SF_4} CF_3\text{-}C{\equiv}C\text{-}CO_2Et$

3. $C_nF_{2n+1}I + HC{\equiv}C\text{-}CO_2Et \xrightarrow{U.V.} C_nF_{2n+1}\text{-}CH{=}CI\text{-}CO_2Et$

$$\xrightarrow{-HI} C_nF_{2n+1}\text{-}C{\equiv}C\text{-}CO_2Et$$

Figure 13

1. Both ethyl 4,4,4-trifluoro-2-butenoate and the corresponding hexenoate have been brominated. The reactions occurred under mild conditions. The dehydrobromination reactions will be carried out, providing reaction 2, with the recent availability of sulfur tetrafluoride, fails. The ethyl acid ester of acetylenedicarboxylic acid has been prepared. 3. Should both reactions 1 and 2 fail, sequence 3 would yield the necessary acetylenic ester. Propiolic acid and its ethyl ester have been prepared. The addition of perfluoropropyl iodide to ethyl propiolate gave a compound expected to be the desired product. It is under investigation.

Diels succeeded in cyclotrimerizing dimethyl acetylenedicarboxylate in pyridine and acetic acid.[14] A similar reactivity of perfluoroalkylacetylenic acid esters is plausible and merits investigation.

Compounds type $C_nF_{2n+1}-C{\equiv}C-C_nF_{2n+1}$ can be prepared quite easily (Figure 14):

$$(R_f-CCl_2-)_2{}^{15} \xrightarrow[\text{EtOH}]{Zn^{16}} R_f-CCl{=}CCl-R_f \xrightarrow[\text{EtOH}]{Zn^{16}} R_f-C{\equiv}C-R_f$$

$R_f = C_nF_{2n+1}$

Figure 14

2,3-Dichloro-1,1,1,4,4,4-hexafluorobutene-2 was prepared. Further dehalogenation was described by Henne and Finnegan, but stipulates a reaction time of 10 days at low temperatures, since the danger of substitution of chlorine by hydrogen is pronounced. An attempt at dechlorination with cuprous chloride failed; Henne's preparation will be referred to, unless, similarly to reaction 2, Figure 13, reaction of the prepared acetylenedicarboxylic acid with sulfur tetrafluoride is successful (Figure 15):

$$HO_2C-C{\equiv}C-CO_2H + SF_4 \longrightarrow CF_3-C{\equiv}C-CF_3$$

Figure 15

Of interest will also be the trifluoropropyne, $CF_3-C{\equiv}CH$ obtainable from the already prepared bromide, $CF_3-CH{=}CHBr$.

The cyclotrimerization of such acetylenes, with no functional groups beside the triple bond, is envisaged by the method of Franzus[17] who carried out reactions with analogous non-fluorinated acetylenes and a Ziegler catalyst.

The second route consists in the metallation of known perfluoroalkylbenzenes. The reaction of benzotrifluoride with n-butyllithium, to give mainly o-trifluoromethylbenzoic acid, is known.[18] p-bis(Trifluoromethyl) benzene (Figure 9) was thus reacted with n-butyllithium in ether,[19] with subsequent carboxylation and hydrolysis. The product isolated was identified as the monocarboxylic acid, 2,5-bis(trifluoromethyl)benzoic acid. The reaction will be repeated under more vigorous conditions, to secure introduction of a second carboxyl group. Further proposed are halogen-metal exchange reactions with the readily available mono- and bis(trifluoromethyl)benzene dibromides and with n-butyllithium,[20] followed by carboxylation and hydrolysis.

The third route deals with the use of sulfur tetrafluoride on benzenepolycarboxylic acids. Thus, pyromellitic acid was exposed to the fluorinating agent and a compound was isolated which is believed to be, on the basis of infrared spectral data, bis(trifluoromethyl)phthalic anhydride. The compound is under further investigation. Complete substitution to tetrakis(trifluoromethyl)benzene will be also attempted, with subsequent metallation, carboxylation and hydrolysis to the highly desirable tetrakis(trifluoromethyl)terephthalic acid (Figure 16):

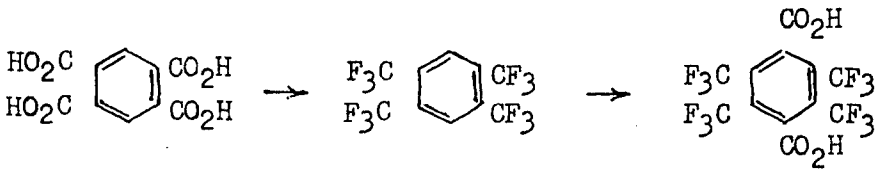

Figure 16

EXPERIMENTAL

1. Heptafluoropropyl Iodide

The silver salt of heptafluoro butyric acid was prepared in 94-96% yield, from which by the Hunsdiecker reaction, the heptafluoropropyl iodide was obtained in 64% yield.

2. Attempted Reaction between Allyl Bromide and Heptafluoropropyl Iodide

60 g. (0.2 mole) of heptafluoropropyl iodide and 60 g. of allyl bromide (0.5 mole) were placed in a 300 mls. three-necked flask, fitted with reflux condenser and stirrer. The contents of the flask were allowed to stir for 110 hours under irradiation with a 100 watt. G. E. Hg lamp, placed at 2 cm. distance. The reaction gave a quantitative recovery of allyl bromide.

3. Preparation of Disilver Perfluoroglutarate

Basic potassium permanganate oxidation of 1,2-dichlorohexafluorocyclopentene gave the dibasic acid in 80-85% yield. Conversion to the disilver salt was achieved in 95% yield.

4. 1,3-Diiodo-1,1,2,2,3,3-hexafluoropropane

Silver perfluoroglutarate (210 g., 0.52 mole) was ground to a fine powder, thoroughly mixed with finely powdered iodine (570 g., 4.5 gram atoms) and placed in a 3-liter, 1-necked flask which was connected to a cold trap cooled with dry ice. The connecting tube was at least 15 mm. in diameter to prevent clogging by the sublimed iodine. The cold trap was connected to a bubble counter so that the reaction could be followed by the evolution of carbon dioxide. The flask was heated with an open flame at such a rate that a smooth, steady evolution of carbon dioxide was maintained. When the carbon dioxide evolution diminished, a vacuum system including an extra dry ice trap replaced the bubble counter and the entire system was slowly reduced to 1 mm. pressure. This removal procedure was repeated 5 times during a 6-hour reaction period. The portions of dark liquid in the cold traps were combined and distilled to give 1,3-diiodo hexafluoropropane. (105 g., 56% yield), b.p. 130-131° C.

5. Preparation of 1,7-Diiodo-3,3,4,4,5,5-hexafluoroheptane

30 g. (0.074 mole) of 1,3-diiodopropane[1] and about 5 g. (0.17 mole) of ethylene were condensed together in a Carius tube, cooled in liquid nitrogen. The tube was sealed and agitated under irradiation from a 100 watt G. E. Hg lamp for 2 days. The solid obtained was recrystallized from an acetone-water mixture. M.p. 71° C Yield = 87%

Anal. Calcd. for $C_7H_8F_6I_2$: C, 18.6; H, 1.77; I, 54.4.

Found: C, 18.49; H, 1.70; I, 55.3.

6. Attempted Thermal Addition of Ethylene to 1,3-Diiodohexafluoropropane

10 g. (.025 mole) of 1,3-diiodohexafluoropropane and about 4 g. of ethylene were placed in a 100 ml. autoclave and 0.2 g. of benzoyl peroxide was added. The autoclave was heated to 120° C. for 21 hours. No ethylene was recovered. From the contents of the autoclave 70% of the starting material was recovered by distillation, the rest being decomposition material.

7. Preparation of 1,6-Diiodo-3,3,4,4-tetrafluorohexane

22 g. (0.062 mole) of 1,2-diiodotetrafluoroethane and 4 g. (0.014 mole) of ethylene were condensed into a Carius tube placed in liquid

nitrogen. The tube was sealed and agitated under irradiation by a U.V. lamp placed at 2 cm. distance. After most of the liquid had solidified, the tube was opened in liquid nitrogen and the solid separated from the liquid. After recrystallization, the solid melted at 114°C.-115°C.

Anal. Calcd. for $C_6H_8F_4I_2$: C, 17.5; H, 1.95; I, 61.9.

Found: C, 17.83; H, 2.18; I, 61.21.

8. Preparation of 3,3,4,4,5,5-Hexafluoroheptane-1,7-diol Diacetate

11.5 g. (0.025 mole) of 1,3-diiodohexafluoropropane, 4.90 g. (.05 mole) of freshly fused potassium acetate and 15 mls. of glacial acetic acid were placed and refluxed for 8 hrs. in a 100 ml. round bottom flask, fitted with a reflux condenser. The contents of the flask were first washed with water to remove any free acid. The water-insoluble layer was dissolved in ether and washed with a 10% sodium carbonate solution and then twice with distilled water. The ethereal solution was dried over anhydrous magnesium sulfate. Upon evaporation of ether, the crude products was distilled. The fraction boiling at 133°C./3 mm. was collected and analyzed.

Yield = 56%; n_D^{23} = 1.3895

Anal.: Calcd. for $C_9H_{14}O_4F_6$: C, 40.7; H, 4.32; F, 35.2.

Found: C, 40.4 g; H, 4.44; F, 35.01.

A low boilding fraction which gives positive tests for carbon and fluorine was also collected. (30% yield calculated for the monoiodoacetate ester.)

9. Preparation of 3,3,4,4,5,5-Hexafluoroheptane-1,7-diol

13 g. (.04 moles) of the diacetate ester and 70 mls. of methanol containing 2 g. of dry HCl were placed in a 100 ml. round bottom flask, fitted with an upright water condenser. Upon refluxing for about 12 hrs., the low boiling material was removed by evaporation and the remainder neutralized with dilute sodium bicarbonate solution and then washed with distilled water. On distillation under vacuum 9 g. of diol was collected at 115°C./1-8 mm.

Yield = 98%; n_D^{21} = 1.3850

Anal.: Calcd. for $C_7H_{10}O_2F_6$: C, 35.00%; H, 4.60; F, 47.5.

Found: C, 35.18; H, 4.52; F, 47.55.

10. Attempted Oxidation of 3,3,4,4,5,5-Hexafluoro-1,7-heptane Diol

30 g. (0.1 mole) of potassium dichromate was dissolved by warming in 100 mls of water containing 39 g. (0.4 mole) of concentrated sulfuric acid.

10 g. (0.042 mole) of diol were placed in a three-necked 200 mls. R. B. flask fitted with a tru-bore stirrer, an upright condenser and a dropping funnel. The dichromate solution was quickly poured into the flask. The reaction was extremely exothermic. After the reaction subsided, the mixture was allowed to reflux for three more hours. The contents of the flask were cooled and extracted with ether. The ethereal solution was treated with 10% sodium hydroxide solution and the aqueous layer was separated. This was again acidified with dil. sulfuric acid and extracted with ether. The ethereal solution was washed with water and dried over anhydrous magnesium sulfate. Upon evaporation of ether a red-brown solid was obtained which was recrystallized 4 times from hot benzene containing traces of acetone, just enough to dissolve the acid. The product was a crystalline white solid. M.p. 173°-174°C. Yield=40%.

N.E. = 116.2 calcd. N.E. = 114

Anal.: Calcd. for $CF_2(CF{=}CHCO_2H)_2$ $C_7H_4O_4F_4$: C, 36.80; H, 1.75; F, 33.33; O, 28.12.

Found: C, 36.53; H, 1.92; F, 33.30; O, 28.25.

11. Preparation of 3,3,4,4,5,5-Hexafluoropimelic Acid

10 g. (0.042 mole) of diol was placed in a 200-ml., 3-necked round bottom flask fitted with reflux condenser, a True-Bore stirrer and a dropping funnel.

30 g. (0.1 mole) of potassium dichromate was dissolved in 100 g. of water containing 39 g. (0.4 mole) of conc. sulfuric acid and placed in the dropping funnel.

The flask was cooled in an ice bath and the dichromate solution was added dropwise. After about 30 minutes stirring was commenced. The ice bath was replaced by a heating mantle and the dropping funnel by a glass stopper. The contents were refluxed overnight. The reaction mixture was cooled and extracted with ether. The solvent was evaporated from the ethereal solution. A solid was obtained which was sublimed under vacuum. It weighed 6 g. M.p. = 165°. Yield = 54%.

Anal.: Calcd. for $C_7H_6O_4F_6$: C, 31.34; H, 2.24; F, 42.54.

Found: C, 31.58; H, 2.50; F, 42.40.

12. Attempted Preparation of the Grignard Reagent of 3,3,4,4,5,5-Hexafluoro-1,7-diiodoheptane

A. A dry 1-l three-necked flask was equipped with mercury seal stirrer, a reflux condenser, dropping funnel and a gas inlet tube for passing dry nitrogen through the system. The condenser outlet was connected to a $CaCl_2$-drying tube. The nitrogen was dried by passing it through a concentrated sulfuric acid bubbler.

6.5 g. (0.26 mole) of pure magnesium metal was introduced into the flask and the apparatus was flamed under a nitrogen flash. 10 mls. of anhydrous ether containing a few drops of methyl iodide was added to start the reaction and then 30 g. (0.06 mole) of 3,3,4,4,5,5-hexafluoro-1,7-diiodoheptane dissolved in 500 ml. of anhydrous ether was added slowly. Every 10 minutes the addition of ether was stopped and the flask heated on a steam bath for a few minutes. After the addition was complete, the mixture was refluxed for an hour on a steam bath. After cooling, the mixture was poured, with constant stirring, on to powdered dry ice in a large beaker. Stirring was continued until all the excess CO_2 had evolved. The mixture was hydrolyzed with 40-50% sulfuric acid. The ether layer was separated and the aqueous layer extracted with ether. The combined ether layers were dried over anhydrous magnesium sulfate and the ether was stripped off. Purification of the viscous residue yielded the starting material.

B. The above experiment was repeated in a similar manner except that tetrahydrofuran was used as solvent. As before, no reaction occurred and the starting material was recovered.

13. Reaction between 3,3,4,4,5,5-Hexafluoro-1,7-diiodoheptane and Potassium Cyanide

In a 200 ml. 3-necked flask fitted with a True-Bore stirrer and a reflux condenser, was placed 22 g. (.04 mole) of hexafluoro-1,7-diiodoheptane dissolved in 45 mls. of acetone. 10 g. (0.14 mole) of potassium cyanide dissolved in 18 ml. of water was added slowly into the flask. The mixture was refluxed and stirred for about 60 hrs. The solvent was evaporated and the residue extracted with ether. The ethereal layer was washed with 2 N sodium hydroxide, sodium thiosulfate and water successively and then dried over anhydrous magnesium sulfate. The ether was removed by evaporation and the residue, on distillation, gave the following 2 fractions:

Cut No.	Temperature	Amount
1	88°-92°C./10 mm.	3 g.
2	92°-94°C./10 mm.	4 g.

Cut No. 2 has a refractive index, $n_D^{25.5} = 1.3700$. The product is being analyzed.

14. Attempted Reaction between Tetrafluoroethylene and the Diacetate of 2-Butyne-1,4-diol

A Carius tube cooled to -110°C was charged with 7.0 g. of tetrafluoroethylene, approximately 0.1 g. of hydroquinone as inhibitor, and 11.9 g. of the diacetate of 2-butyne-1,4-diol. After sealing, the tube was placed in a tube furnace and heated at 150-170°C. for eight hours. The tube was then allowed to cool to room temperature, placed in a cold bath and the seal broken. It was noted that some charring occurred. After collecting the unreacted tetrafluoroethylene and other products, if any, boiling below room temperature, the black residue was distilled under vacuum to give 9.2 g. of starting material, b.p. 94-95/1 mm., $n_D^{20.5} = 1.4540$.

15. Attempted Reaction of Perfluoropropene with Allyl Alcohol

A 100-ml. autoclave was charged with an excess of allyl alcohol and approximately 15 g. of perfluoropropene in the manner cited above. In order to avoid possible polymerization or pyrolysis of the alcohol, the temperature was kept below 190°. The reactants were heated in the autoclave at 180 ± 10°C. for a 36-hour period. A maximum pressure of 300 psi was observed. After cooling and venting the autoclave of all gas, the remaining liquid was distilled. Unreacted allyl alcohol was recovered in this manner. The residue was distilled under vacuum. A small amount of liquid was obtained in this manner, b.p. 75-86°C./20 mm. A lower fraction was also obtained, b.p. 30-32°/20 mm.

16. Attempted Reaction of Perfluoropropene with Allyl Chloride

A. A 100-ml. autoclave was charged with 10.5 g. (0.07 mole) of perfluoropropene and excess of allyl chloride and heated at 140-150°C for a period of eight hours. Only starting material was obtained from this reaction.

B. A 100-ml. autoclave was partially filled with glass beads, 10.5 g. (0.07 mole) of perfluoropropene, an excess of allyl chloride, and heated at 170-180°C. for a period of ten hours. A maximum pressure of 1000 psi was observed. In addition to unreacted perfluoropropene, a gas was given off which gave an acidic reaction.

17. Attempted Reaction between Perfluoropropene and Acrylonitrile

A 100-ml. autoclave was charged with 40 g. of acrylonitrile and 0.5 g. of hydroquinone. Approximately 8 g. of perfluoropropene was added under pressure. In order to have a large total pressure in the system, nitrogen was forced in until the pressure gauge read 1500 psi. The autoclave was heated until the thermocouple indicated 150°C. The reaction mixture was then heated for 12 hours. After the autoclave cooled down to room temperature, the gas was bled off slowly into a dry

ice-trichloroethylene trap in order to collect any unreacted perfluoropropene. When the autoclave was opened, it was discovered that the contents were charred and/or polymerized.

18. Attempted Reaction of 1,1,2-Trichloro-3,3,3-trifluoro-1-propene with Allyl Alcohol

A 100-ml. autoclave was partially filled with glass beads, an excess of 1,1,2-trichloro-3,3,3-trifluoro-1-propene, and approximately 12 g. of perfluoropropene. The temperature was gradually increased. After heating for eight hours at 250-280°C, heating was discontinued. A maximum pressure of 1700 psi was observed. The release valve on the autoclave was opened gradually in order to recover any gas. Only tar and pyrolysis products were obtained from this reaction.

19. Attempted Reactions of Tetrafluoroethylene with 2,3-Dichlorohexafluoro-2-butene

A. A Carius tube was charged with 10 g. (0.1 mole) of tetrafluoroethylene, 23.3 g. of 2,3-dichlorohexafluoro-2-butene and 0.1 g. of hydroquinone. The tube was sealed and placed in a tube furnace and the variac was adjusted to give a temperature of 150-170°C. When the furnace was checked several hours later, the tube was found to have exploded.

B. A 100-ml. autoclave was charged with 23.3 g. (0.15 mole) of 2,3-dichlorohexafluoro-2-butene, 0.1 g. of hydroquinone, flushed with nitrogen and placed in a dry ice-trichloroethylene bath. When cold, the autoclave was evacuated for 80 seconds with an oil pump. A tube containing 15.0 g. of tetrafluoroethylene and a stopper with a glass tube running down to the bottom of the test tube was connected to the autoclave and the material was transferred into the autoclave. The autoclave was heated to 180°C. The maximum recorded pressure was 125 psi. Upon cooling of the autoclave, the contents were removed. No material was found to boil at a higher temperature than that observed for 2,3-dichlorohexafluoro-2-butene. Only 16.8 g. of the latter was recovered from the autoclave.

20. Attempted Reaction of Tetrafluoroethylene with Ethyl Trifluoro-2-butenoate

A Carius tube was charged with 7.5 g. of ethyl trifluoro-2-butenoate and 6.4 g. of tetrafluoroethylene, and a little hydroquinone as inhibitor. The material was heated in a tube furnace at 160°C for a period of 8 hours. After allowing the unreacted tetrafluoroethylene to evaporate, the remainder was distilled. Only starting material was obtained.

21. Attempted Reaction of Tetrafluoroethylene with Furan

A Carius tube was loaded with 10.2 g. (0.15 mole) of furan and a small quantity of hydroquinone. The tube was placed in an ethanol-liquid

nitrogen bath (-110°C) and charged with an approximately equivalent amount of tetrafluoroethylene. The tube was sealed and placed in a tube furnace and heated at 150°C for an eight-hour period. After allowing the tube to cool, it was placed in an ethanol-liquid nitrogen bath and opened. The tube was allowed to warm to room temperature in order to collect the unreacted tetrafluoroethylene. Most of the tetrafluoroethylene was recovered unreacted. Distillation of the residue gave unreacted furan and a small liquid residue.

22. Attempted Reaction of Perfluoropropene with Furan

A Carius tube was charged with 6.8 g. (0.1 mole) of furan, a few crystals of hydroquinone, placed in a dry ice-trichloroethylene bath, and charged with approximately 8 g. of perfluoropropene. The tube was sealed and heated at 180°C. for a period of twenty-four hours. The tube was allowed to cool down to room temperature and then placed in a dry ice-trichloroethylene bath before opening. It appeared, at first, that complete pyrolysis had occurred. The material was chipped and scraped from the tube. No perfluoropropene was recovered, nor was there any liquid present in the tube. Examination of the solid from the tube showed that some pyrolysis had occurred; however, also present, was a rather brittle solid which was dark brown to black and had a very shiny (glazed) surface. When a piece of the material was held in a Bunsen flame, it was seen to burn with a rather smokey flame. A residue was left, and since the reactants did not come in contact with metals at any time, it is apparently carbon. A sodium fusion test on the material indicated the presence of fluorine.

23. Attempted Condensation of Hexafluorobutadiene with Acrylic Acid

The acrylic acid used was stabilized with methylene blue, and no attempt was made to remove this. The usual procedure was followed using 7.2 g. of acrylic acid, 8.1 g. of hexafluorobutadiene and a little peroxide. After sealing the tube the reaction mixture was heated in the tube furnace at 150-160°C. for eight hours, after which time the tube contained, in addition to hexafluorobutadiene, a rubbery-polymeric material. Approximately 100 ml. of water was poured in the Carius tube and allowed to remain in contact for a period of two days. The contents of the tube were filtered, and the filtrate concentrated on a Rinco evaporator. This left only a small amount of a polymeric solid.

24. Reaction of Sulfur Dioxide with Hexafluorobutadiene

A. Approximately 4 g. of hexafluorobutadiene and an excess of sulfur dioxide were placed in a Carius tube and sealed. The tube was allowed to stand for 7 days. The solution became somewhat turbid at first and finally, a white solid precipitated out. When the tube was opened, in addition to recovered starting material, a small amount of an unidentifiable solid was isolated.

B. A Carius tube was charged with 8.1 g. of hexafluorobutadiene and 3-4 g. of sulfur dioxide. The resulting solution (at -78°C.) was yellow. The tube was sealed and heated at 190°C. in a tube furnace for a period of 16 hours. The tube was cooled in a dry ice-trichloroethylene bath, opened, and allowed to warm to room temperature in order to collect any unreacted starting material. A small amount of a brown residue remained. This was distilled to give approximately 0.5 ml. of a colorless substance, b.p. 73°C. (maximum). A sample was submitted for infrared. The recovered material was sealed up again and stored at room temperature in order to see if a sulfone will form. If a sulfone formed during the course of the reaction, it may have been decomposed by the high temperature.

25. Attempted Reaction of Hexafluorobutadiene with Methanol

A metal tube was charged with 15 g. of hexafluorobutadiene, 8 g. of methyl alcohol and 1% by weight of benzoyl peroxide. The closed tube was heated at 90 - 100°C. for a period of ten hours. At the end of this period, the tube was allowed to cool and a valve was opened in order to recover any unreacted hexafluorobutadiene. The contents of the tube were poured into a beaker, and a white solid was filtered off (unreacted peroxide), and some sodium bisulfite was added to destroy any of the unreacted peroxide which might have remained in solution. The material was filtered again. When the methyl alcohol was stripped off, a brown residue remained which was soluble to varying degrees in methanol, acetone and ether, and only slightly soluble in water. An attempt was made to recrystallize the material from aqueous methyl alcohol. This procedure gave a yellowish compound which did not seem to melt completely. Vacuum sublimation gave a white solid, m.p. 105, which seemed to be aromatic on the basis of spectra. The entire sample could not be sublimed. A total of 4 g. of the brown solid was isolated. The product is under investigation.

26. Preparation of 2,3-Dichloro-1,1,1,4,4,4-hexafluoro-2-butene

A 3-l., 3-necked flask was fitted with an open circuit dropping funnel, True-Bore stirrer and distilling head. The flask was charged with 400 ml. of anhydrous dioxane and powdered zinc (32 g., 0.49 moles). The addition funnel was filled with a solution prepared by dissolving 2,2,3,3-tetrachloro-1,1,1-4,4,4-hexafluorobutane (102 g., 0.33 moles) in 300 ml. of dioxane. Stirring was started and the flask was heated to dioxane reflux. The dioxane containing the chlorofluorobutane was added dropwise. During this addition, the apparatus was being flushed out with nitrogen. Two traps were used; the first trap was cooled by means of ice and water, and the second was cooled by a triclene-dry ice mixture. The material in the traps and the other material distilling over between 65-70°C. were collected and redistilled to give 59.2 g. (76.2%) of 2,3-dichloro-1,1,1,4,4,4-hexafluoro-2-butene, b.p. 67°C.; n_D^{20} 1.3459.

27. Reaction of 2,3-Dichloro-1,1,1,4,4,4-hexafluoro-2-butene with Cuprous Chloride

A Carius tube was charged with 10.89 grams of cuprous chloride, 25 ml. of dried benzene and 11.65 g. (0.05 mole) of 2,3-dichloro-1,1,1,4,4,4-hexafluoro-2-butene. The tube was sealed and then heated in a tube furnace at 135°C for eight hours. The tube was allowed to cool to room temperature. After placing the tube in a Dewar containing dry ice, it was opened. The mixture was filtered. Although the solid seemed to change in color, the filtrate did not yield anything except benzene and the starting olefin.

28. Preparation of Ethyl 2,3-Dibromo-4,4,4-trifluorobutyrate

A Carius tube was charged with 24.4 g. (0.14 mole) of ethyl 4,4,4-trifluoro-2-butenoate and 24 g. (0.15 mole) of bromine. The tube was placed in a Dewar condenser containing dry ice and trichloroethylene and sealed. It was then allowed to remain at room temperature for several hours. It was noticed that much of the bromine color had disappeared and the solution was strawberry red in color. The tube was placed in a tube furnace and heated at 100-110°C. for a period of two hours. After allowing the tube to cool, it was placed in a dry ice and trichloroethylene bath and opened. The liquid in the tube was pale yellow. An aqueous solution containing ten percent by weight of sodium bisulfite was added to the liquid. The two layers were separated and the aqueous layer was extracted with ether. The ether extracts and the water-insoluble layer were combined and dried over anhydrous magnesium sulfate. After removal of the magnesium sulfate by filtration, the ether was distilled off on a steam bath. The residue was fractionated to give 24.7 g. (74.2%) of ethyl 2,3-dibromo-4,4,4-trifluorobutyrate, b.p. 96°C./24 mm. n_D^{20} 1.4438 (reported: b.p. 90-92°C./15 mm., n_D^{20} 1.4448).

29. Preparation of Ethyl 2,3-Dibromo-4,4,5,5,6,6,6-heptafluorohexanoate

A. A three-necked flask was fitted with stirrer, condenser and an additional funnel, and charged with 13.4 g. (0.1 mole) of ethyl 4,4,5,5,-6,6,6-heptafluoro-2-hexenoate and 75 ml. of carbon tetrachloride. The solution was heated to reflux with stirring. To the addition funnel was added 8 g. (0.1 mole) of bromine which was added dropwise to the flask. The contents of the flask were heated overnight (ten hours). Since the bromine color was still present, it was decided to add 25 ml. of acetic acid. Refluxing the solution for an additional 4 hours caused the bromine color to disappear. The reaction mixture, after cooling, was poured into 100 ml. of a 10% aqueous sodium bisulfite solution. The water-insoluble material was separated, and the aqueous layer extracted several times with ether. These were combined and dried over anhydrous sodium sulfate. The sodium sulfate was filtered off and the ether

removed by distillation. Distillation of the residue gave fractions boiling in the range 100-130°C./16 mm.

B. Using the same procedure described above for the butyrate, a Carius tube was charged with 14.1 g. (0.05 mole) of ethyl 4,4,5,5,6,6,6-hexafluoro-2-hexenoate and 8.0 g. (0.05 mole) of bromine. However, the reaction was carried out at 110°C. for a six-hour period. The dibromo-ester was obtained in 72% yield, b.p. 102-104°C./15 mm., n_D^{20} 1.4078.

30. Reaction of Ethyl Propiolate with Iodoperfluoropropane

A Carius tube was charged with 7.2 g. (0.0735 mole) of ethyl propiolate and 22 g. of iodoperfluoropropane. The tube was sealed, placed in a horizontal position 14 inches away from a U.V. lamp (G.E. H400-A1), and irradiated for two days. Besides some unreacted iodo-perfluoropropane, 8.3 g. of a product was isolated, b.p. 50°C./0.5 mm. The product was violet in color. However, when the product was distilled from copper powder, a colorless liquid was obtained. The compound is under investigation.

31. Preparation of 1-Bromo-3,3,3-trifluoropropene

A 500-ml., three-necked flask was fitted with a stirrer and a 25 cm. Vigreux column attached to a total reflux distillation head, and an addition funnel. In the flask was placed 175 ml. of absolute ethyl alcohol and 8.5 g. of potassium hydroxide. The solution was heated to reflux and 38.4 g. (0.15 mole) of 1,1-dibromo-3,3,3-trifluoropropane which was added dropwise from the addition funnel to the flask. As the propene formed, it was distilled into a receiver. In this manner, 14.5 g. of 1-bromo-3,3,3-trifluoro-1-propene was obtained, b.p. 38-40°, n_D^{20} 1.3576, reported 39-39.5°C., n_D^{20} 1.3580 (Conversion: 55%).

32. Preparation of Propiolic Acid

The monopotassium salt of acetylenedicarboxylic acid (100 g.; 0.67 mole) was dissolved in 1 liter of water and heated on a steam bath for one-half hour, then heated at reflux for an additional half hour. The cooled solution was acidified with concentrated sulfuric acid and extracted five times with 100 ml. portions of ether, the combined ether layers dried over anhydrous magnesium sulfate and the ether removed by distillation. Distillation of the residue under vacuum yielded 34.5 g. of propiolic acid, b.p. 63-68/20-25 mm. (75% yield).

33. Preparation of Acetylenedicarboxylic Acid

A slurry of 76.1 g. of the monopotassium salt of acetylene dicarboxylic acid in 90 ml. of distilled water was placed in an ice bath and stirred vigorously while concentrated sulfuric acid was added

until the solution remained acidic. The reaction mixture was extracted with five 75 ml. portions of ethyl ether and the combined ether layers were evaporated at room temperature under an air jet. The product was dried overnight in a vacuum dessicator containing concentrated sulfuric acid. The product, a white powder, m.p. 177-178°C., was obtained in 74.5% yield.

34. Preparation of the Ethyl Acid Ester of Acetylenedicarboxylic Acid

In a one-liter round bottom flask was placed a solution of 27 g. of acetylenedicarboxylic acid dissolved in 450 ml. of absolute ethyl alcohol. The solution was heated on a water bath with a reflux condenser for 8 hours. Excess alcohol was evaporated and the residue was neutralized with an alcoholic solution of potassium hydroxide. The ester salt had a low solubility in alcohol and precipitated out. It was dissolved in water, treated with sulfuric acid, and the resulting aqueous solution was repeatedly extracted with ether. The ether extracts were combined and dried over anhydrous magnesium sulfate. The magnesium sulfate was filtered from the mixture and the resulting ether solution was placed on a steam bath and the ether stripped off. Further purification was not carried out at this time.

35. Preparation of 2,5-bis(trifluoromethyl)benzoic Acid

A 500-ml. three-necked flask was fitted with a stirrer and a nitrogen inlet carrying a low-temperature thermometer. The apparatus was flamed out thoroughly while nitrogen was passed through rapidly. The rate of flow of the nitrogen was slowed down and 200 ml. of anhydrous ether was introduced into the flask followed by 8.6 g. (1.25 gram atoms) of lithium wire which had been cut into small pieces. After the addition of the lithium, a dropping funnel was attached which contained a solution of 68.5 g. (0.50 mole) of n-butyl bromide solution was added to the flask under stirring. The mixture was cooled to -15 to -10°C. by immersing the flask in a Dewar condenser which contained a carbondioxide-triclene bath maintained at -30 to -45°C. When the solution became cloudy, the remainder of the n-butyl bromide solution was added dropwise over a period of thirty minutes while the internal temperature was kept at -10 ± 5°C. After addition was complete, the mixture was stirred for an additional two hours while the temperature was allowed to rise to 10°C. in an ice-water bath. From the addition funnel was added dropwise 21.4 g. (0.1 mole) of p-bis(trifluoromethyl)benzene dissolved in 100 ml. of anhydrous ether. After the addition was completed, the bath was removed, and stirring was continued. The reaction became exothermic. When auto-refluxing stopped, the reaction mixture was stirred and refluxed for an additional four hours. The mixture was then poured over finely powdered dry ice. After the excess carbon dioxide had sublimed, 150 ml. of water was added and the ether and water layers were separated. The aqueous layer was extracted with ether. Upon acidification of the

aqueous layer, a precipitate formed immediately. Filtration of this mixture yielded 19 g. (73.6%) of a brown solid. Recrystallization from petroleum ether (b.p. 35-37) gave white needles, m.p. 76-77°C. (uncorr.), N.E.: 253, Calcd. for $C_9H_4O_2F_6$: 258

Anal. Calcd. for $C_9H_4O_2F_6$: C, 41.85; H, 1.55; F, 44.11

Found: C, 41.86; H, 1.55; F, 44.31

36. Reaction of Sulfur Tetrafluoride with Pyromellitic Acid

A. A stainless steel tube was dried and charged with 5.2 g. (0.02 mole) of pyromellitic acid. The tube was placed in a dry ice-trichloroethylene bath and evacuated. It was then charged with 31.4 g. (0.32 mole) of sulfur tetrafluoride. The tube was allowed to warm to room temperature, placed in an oil bath and heated for two-hour periods at each of the following temperatures: 50°C, 80°C and 115-120°C. The tube was allowed to cool to room temperature and then placed in a Dewar containing dry ice and trichloroethylene. The unreacted sulfur tetrafluoride and other gases were collected. Since no liquid product was present in the reaction tube, the tube was left opened overnight to permit the remaining traces of gaseous materials to evaporate. Some fumes were observed after the tube had been opened to the air. The solid recovered contained only traces of fluorine.

B. A stainless steel tube was dried and charged with 2.6 g. (0.01 mole) of pyromellitic acid and the sulfur tetrafluoride recovered from the previous attempt. The tube was heated for four hours at 50-80°C. and then sixteen hours at 150°-160°C. The tube was allowed to cool to room temperature and then placed in a Dewar containing dry ice and trichloroethylene. The unreacted sulfur tetrafluoride and other gases were collected. Some liquid product was obtained this time. The tube was rinsed several times with ether and the extracts combined with the other liquid portion. The ether was stripped off by distillation and the residue distilled under vacuum. Distillation yielded a pale-yellow liquid, b.p. 100-120°C./1.5 mm. Although very efficient fractionation was not possible on such a small sample, three fractions were taken. An infrared spectrum on a sample of this material indicated the presence of an anhydride and the presence of trifluoromethyl groups. The compound, probably 3,4-bis(trifluoromethyl)phthalic anhydride is under investigation.

A portion of the liquid product obtained above was hydrolyzed with aqueous potassium hydroxide. This yielded a solid material. The alkaline solution was acidified with sulfuric acid and the solid material obtained was filtered off. It is currently being investigated.

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